

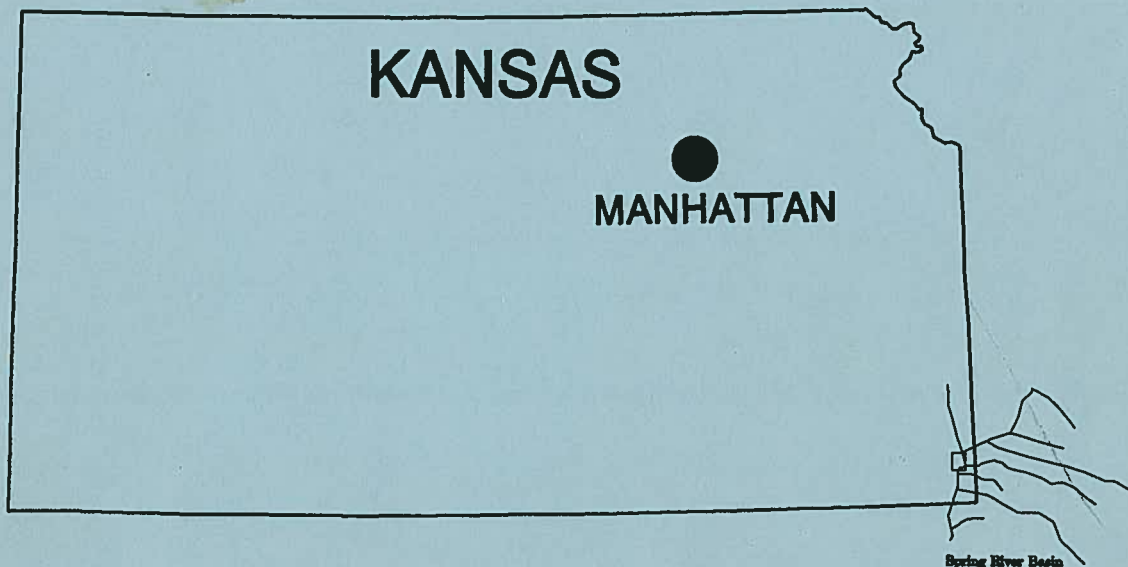
Contaminant Report Number: R6/505M/91



U.S. FISH & WILDLIFE SERVICE  
REGION 6  
CONTAMINANTS PROGRAM



TRACE ELEMENTS AND  
ORGANIC COMPOUNDS IN THE  
SPRING RIVER BASIN OF  
SOUTHEASTERN KANSAS IN 1988



U.S. FISH AND WILDLIFE SERVICE  
Fish and Wildlife Enhancement  
315 Houston Street  
Manhattan, Kansas 66502

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TRACE ELEMENTS AND ORGANIC COMPOUNDS  
IN THE SPRING RIVER BASIN  
OF SOUTHEASTERN KANSAS IN 1988

by

George T. Allen and R. Mark Wilson

U. S. Fish and Wildlife Service  
315 Houston Street  
Manhattan, Kansas 66502

January 1992

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## ABBREVIATIONS AND CONVERSION FACTORS

### Abbreviations

parts per million .....	ppm
parts per billion .....	ppb
milligrams per liter .....	mg/l
micrograms per liter .....	mcg/l
micrograms per gram .....	mcg/g
not detected (i.e. below analytical detection limits) .....	ND
not analyzed (i.e. no test for this element or compound) ....	NA

### Conversions

milligrams per liter .....	ppm
micrograms per liter .....	ppb
micrograms per gram .....	ppm

## SUMMARY

► We sampled sediments and aquatic biota at five locations in the Spring River drainage in southeastern Kansas. The samples were analyzed for metals, organochlorine compounds, and aliphatic hydrocarbons.

► Concentrations of aluminum, arsenic, barium, beryllium, boron, copper, iron, magnesium, mercury, nickel, selenium, strontium, and vanadium in sediments and biota warrant no further studies.

► Cadmium concentrations in Empire Lake and Spring River sediments were very high, but the cadmium was not accumulated by biota of the lake or the river. However, continued monitoring of cadmium in biota of the river is warranted because changes in Ph or other chemical measures of the river or tributary creeks might affect cadmium availability.

► There is lead and zinc contamination at the sampling sites.

► Concentrations of chromium and manganese in one or more samples indicate that continued monitoring of those metals in the Spring River is warranted.

► Chlordane compound concentrations in biota from Cow Creek outside of Pittsburg indicate episodic chlordane contamination.

► Seven fish composites contained a PCB concentration higher than the EPA protection criterion. The highest PCB concentrations were found in Cow Creek and the Spring River arm of Empire Lake. The PCB concentration in the seven composites exceeded the 1984 NCBP mean, but were well below the maximum observed in the NCBP in 1984.

► The total of aliphatic compounds in five fish composites from the Spring River was above the probable level for discernible effects. The aliphatic hydrocarbon concentrations in many of the biota samples indicated recent petroleum contamination.

## ACKNOWLEDGMENTS

Steve Cringan of the Kansas Department of Health and Environment was a great help in sample collection for this study. We thank Dewey Caster, Ronel Finley, Darren Geimausaddle, and Gene Hansmann of the U. S. Fish and Wildlife Service for their help with this work. Dewey Caster, Tom Nash, and Bruce Waddell of the Fish and Wildlife Service provided valuable reviews of drafts of this report. We appreciate their assistance.

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## INTRODUCTION

The discovery of ores containing lead and zinc in Galena, Kansas in 1870 marked the beginning of 100 years of mining for the two metals in southeast Kansas (McCauley *et al.* 1983). Many locations in Cherokee County and nearby in Oklahoma and Missouri have been greatly affected by mining. Today, ore piles, overburden piles, abandoned mines, and collapsed mine tunnels are found in many places in the tri-state mining area. The mines are hazards because of the possibilities for mine collapses, and many of the piles of ore or overburden are high in cadmium, lead, and zinc. Dust can carry metals far from their original locations. Also, the many piles of rock from mines have been used for a variety of purposes, such as gravel for many of the roads in the tri-state area. Normal surface water drainage and the many underground shafts substantially altered surface water infiltration and groundwater flows. Surface and subsurface waters carry the metals far from their original locations. Therefore, the effects of the mining are widespread in both terrestrial and aquatic systems in the tri-state area. Much of Cherokee County is on the National Priority List for cleanup under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA, or Superfund). U.S. Environmental Protection Agency (EPA) cleanup of the areas affected by mining will not be complete for many years.

Human health problems associated with living in the Galena area were reported by Neuberger *et al.* (1990). Surface water quality problems were noted early this century, and most of the creeks in the Cherokee County area have been affected by mining activities (Spruill 1984). Numerous studies have been done in Cherokee County and in nearby areas in Missouri and Oklahoma. The Kansas studies of which we are aware are listed in Appendix 1.

We conducted this preliminary study primarily to determine the concentrations of cadmium, lead, and zinc in sediments and biota of the Spring River, the major body of flowing water in Crawford and Cherokee counties. Although metals related to past mining activities were of the greatest concern, all samples were analyzed for other metals, for chlorinated hydrocarbon compounds, and for aliphatic hydrocarbon compounds. This report provides data on the present levels of many contaminants in the Spring River, and should help to determine research needs of the U. S. Fish and Wildlife Service (Service) and other agencies in areas of past mining.

## STUDY AREA AND METHODS

In the southeast corner of Kansas, including Cherokee County and parts of Bourbon, Crawford, and Labette counties, the low-lying Cherokee Plain and especially the very small area of Ozark Plateau in Cherokee County are extensions of more eastern physiographic areas. The county has been the sole location in which many plant, fish, or wildlife species have been found in Kansas. Numerous federal and/or Kansas endangered, threatened, or candidate<sup>1</sup> species occur in Cherokee County (Table 1).

Important features of the study area and our sampling locations are shown in Figure 1. The Spring River flows out of southwestern Missouri and through Crawford and Cherokee counties, Kansas, and then south to the Lake o' the Cherokees in Oklahoma. Important tributaries of the Spring River in Kansas include Turkey Creek, Short Creek, Shawnee Creek, Shoal Creek, Brush Creek, and Willow Creek. Empire Lake was formed by damming the Spring River and Shoal Creek.

We collected sediments, aquatic insects, crayfish, and fish samples from five locations on 12 and 13 July 1988 (Table 2). We attempted to collect the same species in each location, but we were unable to do so. All sediment and invertebrate composites were placed in chemically clean jars and frozen. Each fish was measured, weighed, and double wrapped in aluminum foil. All samples were kept on ice in the field. Thereafter, they were frozen until they were prepared for analysis. We considered aluminum contamination from wrapping samples in foil to be negligible. Samples were submitted to the analytical laboratories in September through November 1988. The last results of laboratory analyses were received in December 1989.

Arsenic, mercury, selenium, and other metals were analyzed by the Environmental Trace Substances Research Center (ETSRC) of the University of Missouri. Total arsenic, mercury, and selenium were analyzed using atomic absorption spectroscopy. Detection limits were 0.20 mcg/g for arsenic and selenium and 0.10 mcg/g for mercury. Sediments were analyzed using induction coupled plasma emission spectroscopy (ICP) without preconcentration to test for aluminum, barium, beryllium, boron, cadmium, chromium, copper, iron, lead, magnesium, manganese, molybdenum, nickel, silver, strontium, tellurium, vanadium, and zinc. The insect, crayfish, and fish samples were analyzed by ICP with preconcentration at pH6 to enhance detection of cadmium, lead, and zinc. Other metals determined by ICP in invertebrates and fish were aluminum, beryllium,

---

<sup>1</sup> Under consideration for federal endangered species listing.

Table 1. Endangered, threatened, and candidate species in Cherokee County.

<u>Species</u>	<u>Habitats</u>	<u>Listing Authority and Status<sup>a</sup></u>
<u>Aquatic Invertebrates</u>		
Clanton's Cave Amphipod ( <u>Stygobromus clantoni</u> )	caves and wells	U.S. (C)
Western Fanshell ( <u>Cyprogenia aberti</u> )	Spring River	U.S. (C)
Neosho Mucket ( <u>Lampsilis rafinesqueana</u> )	Spring River	U.S. (C)
Ouachita Kidney-shell ( <u>Ptychobranchus occidentalis</u> )	Spring River	U.S. (C)
<u>Fish</u>		
Neosho Madtom ( <u>Noturus placidus</u> )	Spring River	U.S. (T), Kansas (T)
Arkansas Darter ( <u>Etheostoma caeruleum</u> )	Spring River, Shoal Creek, other creeks	U.S. (C), Kansas (T)
Plains Topminnow ( <u>Fundulus sciadicus</u> )	streams, wetlands	U.S. (C)
Redspot Chub ( <u>Nocomis biguttatus</u> )	Spring River, creeks	Kansas (T)
<u>Amphibians</u>		
Cave Salamander ( <u>Eurycea lucifuga</u> )	caves, springs in forested areas	Kansas (E)
Central Newt ( <u>Notophtalmus viridescens louisianensis</u> )	ponds, small lakes, marshes, ditches	Kansas (T)
Dark-sided Salamander ( <u>Eurycea longicauda melanopleura</u> )	moist areas near streams, in or near caves	Kansas (T)
Graybelly Salamander ( <u>Eurycea multiplicata griseogaster</u> )	cave springs or streams with rock crevices	Kansas (E)
Grotto Salamander ( <u>Typhlotriton spelaeus</u> )	cave streams	Kansas (E)
Eastern Narrowmouth Toad ( <u>Gastrotrane carolinensis</u> )	moist woodland areas	Kansas (T)
Northern Crawfish Frog ( <u>Rana areolata circulosa</u> )	poorly drained lowland meadows	Kansas (T)
Leopard Frog ( <u>Rana pipiens</u> )	all aquatic areas	U.S. (C <sup>b</sup> )
Green Frog ( <u>Rana clamitans melanota</u> )	streams, backwaters, impoundments	Kansas (T)
Northern Spring Peeper ( <u>Pseudacris crucifer</u> )	small ponds or pools near woodlands	Kansas (T)

Table 1 (continued). Endangered, threatened, and candidate species in Cherokee County.

<u>Species</u>	<u>Habitats</u>	<u>Listing Authority and Status<sup>a</sup></u>
<u>Reptiles</u>		
Alligator Snapping Turtle ( <u>Macrolemmys temminckii</u> )	Spring River	U.S. (C)
Northern Redbelly Snake ( <u>Storeria occipitomaculata</u> )	woodlands	Kansas (T)
Texas Horned Lizard ( <u>Phrynosoma cornutum</u> )	sandy grasslands	U.S. (C)
<u>Mammals</u>		
Gray Bat ( <u>Myotis grisescens</u> )	possibly in caves or mine shafts	U.S. (E), Kansas (E)
Eastern Spotted Skunk ( <u>Spilogale putorius interrupta</u> )	woodlands, rocky grasslands	U.S. (C <sup>b</sup> ), Kansas (T)
<u>Birds</u>		
Bald Eagle ( <u>Haliaeetus leucocephalus</u> )	riparian areas	U.S. (E), Kansas (E)
Migrant Loggerhead Shrike ( <u>Lanius ludovicianus migrans</u> )	grasslands and shrublands	U.S. (C)
Henslow's Sparrow ( <u>Ammodramus henslowii</u> )	grasslands	U.S. (C <sup>b</sup> )
Cerulean Warbler ( <u>Dendroica cerulea</u> )	riparian woodlands	U.S. (C <sup>b</sup> )
<u>Terrestrial Plants</u>		
Royal Catchfly ( <u>Silene regia</u> )	grasslands, open woods	U.S. (C)
Weak Nettle ( <u>Urtica chamaedryoides</u> )	riparian woodlands	U.S. (C)
Baldgrass ( <u>Sporobolus ozarkanus</u> )	grasslands, open areas	U.S. (C)
Spikerush ( <u>Eleocharis wolfii</u> )	wetlands, riverine areas	U.S. (C)
Globe Mallow ( <u>Sphaeralcea angusta</u> )	rocky grasslands	U.S. (C)
Gerardia ( <u>Agalinus skinneriana</u> )	grasslands, open woods	U.S. (C)

<sup>a</sup> E - endangered, T - threatened, C - candidate.

<sup>b</sup> Recommended for addition to the candidate species list.

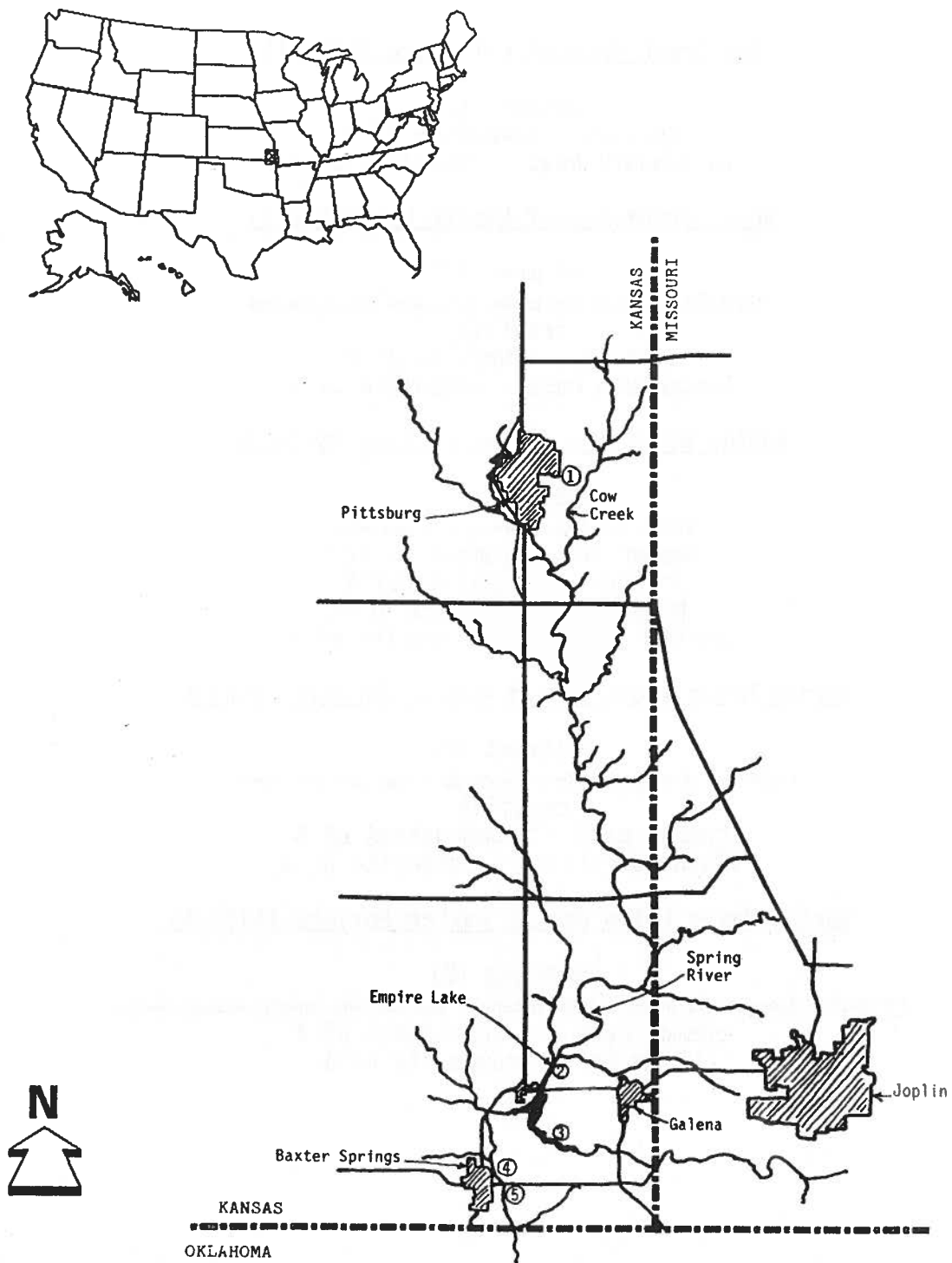


Table 2. Samples collected in Cherokee County for analyses.

Cow Creek east of Pittsburg (Site 1)

sediment (2)  
sunfish - composite of 4  
largemouth bass - composite of 4

Shoal Creek Arm of Empire Lake Site 2)

sediment (2)  
insects (hellgrammites, beetles, trichoptera, giant water bug)  
crayfish  
sunfish - composite of 2  
largemouth bass - composite of 4

Spring River arm of Empire Lake (Site 3)

sediment (2)  
insects (mayfly larvae, whirlygig beetles)  
common carp - composite of 2  
crappie - composite of 4  
bluegill - composite of 4  
channel catfish - composite of 4

Spring River above dam at Baxter Springs (Site 4)

sediment (2)  
insects (trichoptera, riffle and whirlygig beetles, giant water beetle)  
crayfish  
common carp - 2 composites of 4  
flathead catfish - composite of 2

Spring River below dam at Baxter Springs (Site 5)

sediment (2)  
insects (hellgrammites, mayfly nymphs, stonefly nymphs, damselfly nymphs, whirlygig beetles)  
common carp - 2 composites of 4  
white bass - composite of 4



cadmium, chromium, copper, iron, lead, manganese, nickel, tellurium, and zinc.

Detection limits for metals analyzed by ICP are shown in Table 3. ETSRC reported dry weight concentrations for all metals. Wet weight concentrations were calculated by multiplying the dry weight concentration by  $[1 - (\% \text{ moisture}/100)]$ .

The samples were analyzed for chlorinated hydrocarbon compounds and aliphatic hydrocarbons by The Mississippi State Chemical Laboratory (MSCL, Table 4). Concentrations of chlorinated hydrocarbon compounds were determined using electron capture gas chromatography. Concentrations of aliphatic hydrocarbons were determined using capillary column flame ionization gas chromatography. Wet weight detection limits for organics were 0.01 mcg/g for organochlorine pesticides and aliphatics, and 0.05 mcg/g for PCBs and toxaphene. Wet weight concentrations were reported for chlorinated hydrocarbons and for aliphatic hydrocarbons. Lipid-normalization of organic compounds provides no improvement in data reporting (Huckins *et al.* 1988, Schmitt *et al.* 1990), so we did not report lipid concentrations.

No anomalies were reported in the samples. Each sample collected was large enough for the laboratory to determine the concentration of each element or compound at the limit of the analytical equipment. Laboratory quality control was reviewed by the Patuxent Analytical Control Facility (PACF) of the Service. Precision and accuracy of the laboratory analyses were confirmed with procedural blanks, duplicate analyses, test recoveries of spiked materials, and reference material analyses. Round-robin tests among Service and contract analytical labs also were part of the quality control.

Duplicate analyses for arsenic, mercury, and selenium had a maximum difference of 20.0% of the lower concentration (0.10 mcg/g) in one analysis for selenium. Duplicate ICP analyses differed by 16.3% or less, except for one analysis of chromium, which differed by 60.9% of the lower concentration (the difference was 14 mcg/g) and one analysis for beryllium, which differed by 100% (0.01 mcg/g). However, the beryllium concentrations were at the limit of detection in the duplicate analyses. Spike recoveries for metals ranged from 88% to 110% for arsenic, mercury and selenium, and from 76% to 125% for ICP analyses. Residue values were not adjusted on the basis of these recoveries. Results from analyses of reference standards differed from the expected values by 19.1% of the value or less, with the exceptions of an analysis for aluminum (73.8%), and an analysis for nickel (138.5%, but only 0.36 mcg/g).

Duplicate organics analyses differed by no more than 0.01 mcg/g (50%) for organochlorines. The largest percentage difference for aliphatic hydrocarbon duplicates was 50% (0.01 mcg/g). The largest

Table 3. Estimated detection limits for metals in Cherokee County analyzed by ICP. Concentrations are in mcg/g dry weight.

Element	Sediment	Invertebrates and Fish
aluminum	3.0	0.3-0.4
barium	9.0	NA <sup>a</sup>
beryllium	0.1	0.01
boron	2.0	NA
cadmium	0.2	0.03-0.04
chromium	1.0	0.1
copper	0.3-1.0	0.02-0.06
iron	1.0	0.09-0.4
lead	4.0-5.0	0.5-1.0
magnesium	0.1	NA
manganese	0.3-0.4	0.03-0.07
molybdenum	2.0-3.0	NA
nickel	2.0-3.0	0.2-0.4
silver	2.0	NA
strontium	0.1	NA
tellurium	6.0-8.0	0.8-2.0
vanadium	0.3-0.4	NA
zinc	0.3-0.4	0.02-0.08

absolute difference was 0.1 mcg/g (4.2%). Spike recoveries for chlorinated hydrocarbons ranged from 61% to 110%. Spike recoveries for aliphatic hydrocarbons ranged from 11% for one recovery of n-dodecane to 110% for one recovery of pristane; most recoveries were between 51% and 92%. Organic compound data were not adjusted to reflect spike recoveries. Tests of reference standards were not done for organic compounds.

We report element concentrations in mcg/g dry weight. Concentrations of chlorinated hydrocarbons and aliphatic hydrocarbons are reported in mcg/g wet weight. Concentrations of contaminants in samples collected for this study were compared to concentrations found in other studies. We made no attempt to assess the interactions of various contaminants, even though many are known to affect the toxicity of other elements or compounds.

Table 4. Chlorinated hydrocarbons analyzed in Cherokee County Samples.  
Concentrations are in mcg/g wet weight.

Compound	Detection Limit
alpha-BHC	0.01
beta-BHC	0.01
delta-BHC	0.01
gamma-BHC	0.01
Oxychlordane	0.01
cis-Chlordane	0.01
trans-Chlordane	0.01
cis-Nonachlor	0.01
trans-Nonachlor	0.01
Heptachlor Epoxide	0.01
Dieldrin	0.01
Endrin	0.01
o,p'-DDT	0.01
p,p'-DDT	0.01
o,p'-DDE	0.01
p,p'-DDE	0.01
o,p'-DDD	0.01
p,p'-DDD	0.01
Hexachlorobenzene	0.01
Total PCBs	0.05
Toxaphene	0.05
Mirex	0.01

## RESULTS AND DISCUSSION

### METALS

#### Metals Analyzed by AAS

Results of the arsenic, mercury, and selenium analyses are shown in Table 5.

#### Arsenic

There are limited data available on the biological need for arsenic or on its properties that affect animal life. At very low levels, arsenic or arsenic compounds may improve health and growth in animals, and inorganic arsenic can protect against harmful effects of inorganic selenium (Eisler 1988a). However, the different forms of arsenic are poisonous at low concentrations, although the relative toxicities differ (Eisler 1988a, Murphy 1981, Spehar *et al.* 1980). Further, the effects of arsenic may be intensified by exposure to cadmium or lead. Arsenic can be converted to organic forms by methylating bacteria (Hodson 1988). Methylated selenium compounds are made much more toxic by inorganic arsenic compounds (Eisler 1988a, p. 11). Exposure to arsenic, however, increases later tolerance to arsenic in many animals (Eisler 1988a). Phillips and Russo (1978) considered arsenic to have a low bioaccumulation tendency in freshwater fish muscle. Other studies also indicated that arsenic has a low bioaccumulation<sup>2</sup> and biomagnification potential in fish (U. S. Environmental Protection Agency [EPA] 1980a, Spehar *et al.* 1980, Wagemann *et al.* 1978, Winger *et al.* 1990). In addition, arsenic usually is rapidly excreted after exposure (Eisler 1988a).

The mean for arsenic concentrations in soils of the conterminous United States, as determined by Shacklette and Boerngen (1984), was 7.2 mcg/g dry weight, a concentration similar to those found by earlier researchers. The range of values Shacklette and Boerngen found was from less than 0.1 to 97 mcg/g, also the range found in the U.S. west of the 96th meridian. The geometric mean for the western U.S. was 5.5 mcg/g. For the eastern U.S. the mean was 4.8 mcg/g and the range of values was from less than 0.1 to 73 mcg/g. Severson and Tidball (1979) found that arsenic concentrations in soils of the northern Great Plains ranged

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<sup>2</sup> Bioconcentration is the accumulation of an element or compound by an aquatic organism directly from the water. Bioaccumulation is accumulation from water and from food. Biomagnification refers to increases in body burden of an element or compound in successively higher trophic levels (Beyer 1986, Biddinger and Gloss 1984, Hall and Burton 1982, Macek *et al.* 1979, Rand and Petrocelli 1985).

Table 5. Arsenic, mercury, and selenium concentrations in Cherokee County Samples.

Sample	Percent Moisture	Concentration (mcg/g)					
		Arsenic		Mercury		Selenium	
		Dry Weight	Wet Weight	Dry Weight	Wet Weight	Dry Weight	Wet Weight
<u>Cow Creek east of Pittsburg</u>							
Sediment	32.7	4.30	2.89	0.03	0.02	0.30	0.20
Sediment	42.4	9.80	5.64	0.097	0.06	0.60	0.35
Crayfish	71.5	0.79	0.23	0.052	0.01	1.40	0.40
Sunfish	75.5	ND	ND	0.18	0.04	2.00	0.49
Largemouth Bass	73.8	ND	ND	0.36	0.09	2.50	0.66
<u>Spring River arm of Empire Lake</u>							
Sediment	45.6	6.00	3.26	0.45	0.24	ND	ND
Sediment	48.5	3.30	1.70	0.45	0.23	ND	ND
Insects	82.1	0.65	0.12	0.11	0.02	2.40	0.43
Crayfish	70.0	0.30	0.09	0.03	0.01	1.30	0.39
Common Carp	73.7	0.10	0.03	0.042	0.01	1.80	0.47
Channel Catfish	76.8	ND	ND	0.073	0.02	1.60	0.37
Crappie	76.0	ND	ND	0.077	0.02	1.00	0.24
Bluegill	75.6	ND	ND	0.085	0.02	1.30	0.32
<u>Shoal Creek arm of Empire Lake</u>							
Sediment	49.8	2.90	1.46	0.13	0.07	0.40	0.20
Sediment	48.5	2.60	1.34	0.13	0.07	0.30	0.15
Insects	77.4	0.42	0.09	0.036	0.01	3.50	0.79
Crayfish	70.6	0.84	0.25	0.028	0.01	1.10	0.32
Sunfish	75.3	ND	ND	0.05	0.01	2.10	0.52
Largemouth Bass	75.8	ND	ND	0.073	0.02	2.10	0.51
<u>Above the dam at Highway 166 just east of Baxter Springs</u>							
Sediment	34.0	3.40	2.24	0.075	0.05	ND	ND
Sediment	34.9	3.30	2.15	0.29	0.19	0.50	0.33
Insects	74.7	0.30	0.08	0.072	0.02	2.60	0.66
Crayfish	76.6	1.40	0.33	0.036	0.01	0.98	0.23
Common Carp	75.1	0.10	0.02	0.092	0.02	1.60	0.40
Common Carp	76.0	0.20	0.05	0.18	0.04	2.70	0.65
Flathead Catfish	80.2	ND	ND	0.19	0.04	1.40	0.28
<u>Below the dam at Highway 166 just east of Baxter Springs</u>							
Sediment	23.3	5.80	4.45	0.093	0.07	ND	ND
Sediment	27.5	3.90	2.83	0.21	0.15	ND	ND
Insects	73.3	3.30	0.88	0.054	0.01	1.80	0.48
Crayfish	73.2	2.10	0.56	0.03	0.01	0.92	0.25
Common Carp	77.9	ND	ND	0.04	0.01	0.83	0.18
Common Carp	77.2	ND	ND	0.11	0.03	1.50	0.34
White Bass	72.4	0.58	0.16	0.098	0.03	1.90	0.52

from less than 0.1 to 26 mcg/g dry weight, with a geometric mean of 7.1 mcg/g. Martin and Hartman (1984) tested sediments in wetlands of the northern prairie region of the U.S., and found mean dry weight concentrations from 1.9 mcg/g to 12 mcg/g. The mean for pothole locations was 4.4 mcg/g; for riverine sites it was 2.4 mcg/g. Severson *et al.* (1987) sampled sediments at nine Department of the Interior drainwater study sites in the western United States, and found concentrations of 2.4 to 15 mcg/g dry(?) weight.

Most arsenic concentrations in sediments sampled for this study were less than the mean values for other studies. The 9.8 mcg/g value from Cow Creek is the only value above the means from other studies of uncontaminated areas, and is within the range that probably can be considered the norm.

Background arsenic concentrations in freshwater aquatic biota normally are less than 1 mcg/g fresh weight (Eisler 1988a). Different studies have supported this assertion. All arsenic concentrations in aquatic invertebrates we sampled were within the range considered normal by Eisler (1988a). All concentrations in fish samples were below the means from the National Contaminant Biomonitoring Program (NCBP) from 1976 through 1984 (Lowe *et al.* 1985, May and McKinney 1981, Schmitt and Brumbaugh 1990, Walsh *et al.* 1977). Arsenic concentrations measured in this study also indicate that there is little or no arsenic bioconcentration in biota.

### Mercury

Mercury is an extremely toxic nonessential metal. It is a teratogen, a mutagen, and a carcinogen. Mercury has been used for different purposes in agriculture, but industrial processes are now probably the most important sources of mercury contamination. Man-made reservoirs also have led to increased mercury levels in fish because mercury is released from flooded soils to the water (Eisler 1987). However, Phillips *et al.* (1987) found that reservoirs may limit exposure of fish below reservoirs to mercury that is mobilized during flooding. Mercury and its organic forms may persist for many years after sources of pollution are stopped. Mercury can be bioconcentrated and biomagnified in food chains (Eisler 1987, Elliott and Griffiths 1986, Jernelov and Lann 1971, Johnels *et al.* 1967, Phillips *et al.* 1980, Rada *et al.* 1986, Rudd and Turner 1983), effects that are increased by methylation (Hodson 1988). Elemental mercury in aquatic systems was long thought to be biologically unavailable, but anaerobic bacteria can methylate elemental mercury in aquatic systems (Jernelov *et al.* 1969, Johnels *et al.* 1967). Methylmercury has a high potential for bioaccumulation (Phillips and Russo 1978).

Eisler (1987) reported that sediments from uncontaminated lakes

usually contain less than 1 mcg of mercury per gram. Martin and Hartman (1984) found a maximum concentration of 0.11 mcg/g in wetlands of the north-central U.S. Similar concentrations have been found in other studies of uncontaminated sites (e.g. Kent and Johnson 1979, Martin and Hartman 1984, Mathis and Kevern 1975, Price and Knight 1978, Speyer 1980). However, mercury contamination of aquatic systems is long-lasting, and many sites today are affected by activities long past. For example, Richins and Risser (1975) and Cooper (1983) demonstrated the long-term effects of mercury from past mining on the Carson River and Lahontan Reservoir in Nevada; Powell (1983) reported on long-term effects of mercury on the Holston River in Virginia; and mercury in the upper Wisconsin River was studied by Rada et al. (1986).

Probably because invertebrates are of less importance to human health, relatively few studies have analyzed mercury concentrations in invertebrates. Rada et al. (1986) found mean dry weight concentrations of 0.07 to 0.80 mcg/g in crayfish in the upper Wisconsin River. Concentrations in the section farthest downstream were significantly higher than concentrations upstream; up to 1.11 mcg/g. Naturally-occurring mercury apparently affected concentrations in crayfish from the reference area, which were higher than concentrations farther downstream. In aquatic invertebrates exposed to continuous input of 0.8 mcg/l mercury in an artificial stream, total mercury concentrations ranged from less than 1 mcg/g wet weight in water boatmen to over 23 mcg/g in damselflies (Coenagrionidae) (Cox et al. 1975). Pond snails (Physidae) had lower concentrations than the odonates, but still contained up to 8.2 mcg/g. The authors found significant declines in inorganic mercury concentrations in biota two weeks after the mercury input was stopped, but concentrations of methylmercury did not decline. Crayfish (*Cambarus* spp. and *Oronectes* spp.) in 13 lakes in south-central Ontario lakes unaffected by mercury discharges contained from 0.022 to 0.614 mcg of mercury per gram, wet weight (Allard and Stokes 1989). The authors concluded that mercury content in crayfish in the lakes was related to mineralization of the water and to acidification. They suggested that crayfish would be useful in biomonitoring of mercury.

Huckabee et al. (1974) reported that background mercury concentrations in whole fish should be 0.02 to 0.2 mcg/g. Mercury concentrations in fish from the Spring River drainage were not elevated compared to concentrations in fish analyzed for the National Pesticide Monitoring Program (Henderson et al. 1972), in which whole body wet weight mercury concentrations in fish from across the United States ranged from below the 0.05 mcg/g detection limit to 1.25 mcg/g in 1969 and from below the detection limit to 1.80 mcg/g in 1970. Nor were concentrations in fish we collected elevated compared to those in fish collected for the NCBP (Lowe et al. 1985, May and McKinney 1981, Schmitt and Brumbaugh 1990, Walsh et al. 1977).

Mercury concentrations in all sample media we collected were very

low. Our collections indicate that mercury contamination is not a problem in the Spring River drainage.

### Selenium

Selenium is an essential trace nutrient for terrestrial and freshwater organisms (Frost and Ingvaldstad 1975, Marier and Jaworski 1983, Wilber 1980). However, proper selenium levels in animals fall within narrow ranges, and the acute and chronic effects of organic and inorganic forms of selenium differ on aquatic and terrestrial plants and animals (EPA 1987, Lemly 1987). Selenium deficiency and selenium toxicosis can produce a variety of symptoms, many of which are the same (Marier and Jaworski 1983). Numerous cases of selenium poisoning of fish, mammals, and birds have been documented (e.g. Clark 1987, Cumbie and Van Horn 1978, EPA 1987, Hoffman *et al.* 1988, Lemly 1987, Ohlendorf *et al.* 1986a,b, 1988, Saiki and Lowe 1987). In contrast, selenium can reduce the toxic effects of arsenic, mercury, and some other environmental contaminants (EPA 1987).

Habitat variables play a large role in selenium availability (Lemly and Smith 1987). Selenium bioaccumulation and selenium biomagnification occur in some settings (Baumann and Gillespie 1986, Cherry and Guthrie 1977, DuBow 1989, Lemly 1985, 1987, Lemly and Smith 1987, Saiki 1986). However, Adams and Johnson (1977) and Kay (1984) believed that selenium biomagnification does not occur. Phillips and Russo (1978) considered selenium to have a low tendency to bioaccumulate. Besser *et al.* (1989) found that the form of selenium had a great effect on bioaccumulation and toxicity. Organic selenomethionine had a greater toxic effect, a finding also reported by others (e.g. Eisler 1985a, Kleinow and Brooks 1986). Hodson (1988) reported that dietary selenium is much more toxic than waterborne selenium to fish. Size and age make little difference in selenium concentrations in common carp, which accumulate selenium only moderately (Cumbie and Van Horn 1978, Baumann and May 1984).

Lemly and Smith (1987) recommended a 4 mcg/g dry weight level of concern in sediment for protection of fish and wildlife. The geometric mean sediment concentration for soils of the western United States reported by Shacklette and Boerngen (1984) was 0.23 mcg/g dry weight. Severson and Tidball (1979) found a mean of 0.45 mcg/g mean for the northern Great Plains. The means for pothole ( $x=0.89$  mcg/g dry weight, range 0.13 to 2.1) and riverine ( $x=0.52$ , range 0.03 to 5.1) wetlands in the north-central United States were reported by Martin and Hartman (1984). Selenium concentrations in sediments we collected were low (Table 5). Spring River basin concentrations were less than the mean for riverine areas sampled by Martin and Hartman (1984), and well below the level of concern in sediments (Lemly and Smith 1987).

The dry weight selenium concentration of concern for fish and



waterfowl foods recommended by Lemly and Smith (1987) is 5 mcg/g. Invertebrates (insects, plankton, soft parts of mussels and clams) from uncontaminated sites should contain 4.0 mcg/g dry weight or less, or 0.7 mcg/g wet weight or less (Adams and Johnson 1977, Heit et al. 1980, Ohlendorf et al. 1986b, Saiki 1986, Saiki and Lowe 1987, Winger et al. 1984). All selenium concentrations in crayfish and other aquatic invertebrate samples collected from the Spring River and from Cow Creek were within the range that can be considered normal background concentrations, and all were well below 5 mcg/g dry weight.

Nationwide geometric means for selenium concentration in fish collected for the NCBP ranged from 0.48 mcg/g wet weight in 1978-1979 to 0.42 mcg/g in 1984 (Lowe et al. 1985, May and McKinney 1981, Schmitt and Brumbaugh 1990, Walsh et al. 1977). Comparable 85th percentile concentrations were 0.70, 0.71, and 0.73 mcg/g. Some of the fish samples we collected from the Spring River drainage were above the NCBP mean concentrations, but below the 85th percentile concentrations. However, in no sample was the 2 mcg/g wet weight level of concern suggested by Baumann and May (1984) exceeded, and dry weight concentrations were well below the 12 mcg/g dry weight whole body value suggested as a level of concern for reproductive failure of Lemly and Smith (1987).

Selenium concentrations in media collected for this study were not elevated. The concentrations found indicate that selenium exposure is not a problem in the areas that we sampled.

#### Metals Analyzed by ICP

Metal concentrations determined with ICP are shown in Table 6. Molybdenum, silver, and tellurium were below the detection limits of the ICP scans for all analyses.

#### Aluminum

Aluminum is abundant in the earth's crust, but normally is found in water at concentrations less than 1 mcg/l. Shacklette and Boerngen (1984) reported a mean aluminum concentration in soils of 72,000 mcg/g. However, toxicity is greatly affected by its complex chemistry, its form in water, water chemistry (especially pH), and life stage of the organism being studied (e.g. Baker and Schofield 1982, Hunter et al. 1980, Hunn et al. 1987, Palawaski et al. 1989, Palmer et al. 1989). Hall et al. (1985) suspected that high aluminum concentrations and water softness in a Chesapeake Bay tributary contributed to mortality of larval striped bass.

Aluminum has a high tendency to bioaccumulate (Phillips and Russo

Table 6. Element concentrations in Cherokee County samples from ICP scans.

Sample	Element Concentration (mcg/g)									
	Aluminum		Barium		Beryllium		Boron		Cadmium	
	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet
<u>Cow Creek east of Pittsburg</u>										
Sediment	31100	20930	191	129	1.3	0.875	8.0	5.4	1.0	0.67
Sediment	33200	19123	246	142	1.4	0.806	9.3	5.4	1.3	0.75
Crayfish	748	213	NA	NA	0.04	0.012	NA	NA	0.08	0.02
Largemouth Bass	36.8	10	NA	NA	0.01	0.003	NA	NA	0.06	0.02
Sunfish	127	31	NA	NA	0.02	0.005	NA	NA	0.22	0.05
<u>Spring River arm of Empire Lake</u>										
Sediment	28000	15232	199	108	1.1	0.60	7.4	4.0	26.0	14.14
Sediment	28000	14420	198	102	1.1	0.57	7.0	3.6	26.9	13.85
Invertebrates	2940	526	NA	NA	0.13	0.02	NA	NA	2.8	0.50
Crayfish	360	108	NA	NA	ND	ND	NA	NA	1.6	0.48
Common Carp	163	43	NA	NA	0.02	0.005	NA	NA	0.43	0.11
Channel Catfish	210	49	NA	NA	0.02	0.005	NA	NA	0.34	0.08
Crappie	90.5	22	NA	NA	0.02	0.005	NA	NA	0.14	0.03
Bluegill	13	3	NA	NA	0.02	0.005	NA	NA	0.18	0.04
<u>Shoal Creek arm of Empire Lake</u>										
Sediment	12300	6175	109	55	0.77	0.387	ND	ND	23.7	11.90
Sediment	11600	5974	106	55	0.72	0.371	ND	ND	23.2	11.95
Insects	1510	341	NA	NA	0.07	0.016	NA	NA	2.8	0.63
Crayfish	461	136	NA	NA	0.03	0.009	NA	NA	1.6	0.47
Sunfish	88.8	22	NA	NA	0.02	0.005	NA	NA	0.24	0.06
Largemouth Bass	19	5	NA	NA	0.02	0.005	NA	NA	0.09	0.02
<u>Above the dam at Highway 166 just east of Baxter Springs</u>										
Sediment	32200	21252	191	126	1.3	0.86	9.2	6.1	13.0	8.58
Sediment	36100	23501	202	132	1.5	0.98	9.8	6.4	82.7	53.84
Insects	706	179	NA	NA	0.04	0.01	NA	NA	1.0	0.25
Crayfish	1730	405	NA	NA	0.07	0.02	NA	NA	1.1	0.26
Common Carp	198	49	NA	NA	0.02	0.005	NA	NA	1.0	0.25
Common Carp	167	40	NA	NA	0.02	0.005	NA	NA	2.1	0.50
Flathead Catfish	51.2	10	NA	NA	0.01	0.002	NA	NA	0.31	0.06
<u>Below the dam at Highway 166 just east of Baxter Springs</u>										
Sediment	18500	14190	123	94	0.87	0.67	6.0	4.6	14.0	10.7
Sediment	30700	22258	211	153	1.4	1.02	9.1	6.6	25.0	18.1
Insects	3060	817	NA	NA	0.3	0.08	NA	NA	1.5	0.4
Crayfish	1680	450	NA	NA	0.29	0.08	NA	NA	1.2	0.3
Common Carp	104	23	NA	NA	0.01	0.002	NA	NA	0.29	0.1
Common Carp	31	7	NA	NA	0.02	0.005	NA	NA	0.91	0.2
White Bass	19	5	NA	NA	0.01	0.003	NA	NA	0.05	0.01

Table 6 (continued). Element concentrations in Cherokee County samples from ICP scans.

Sample	Element Concentration (mcg/g)							
	Chromium		Copper		Iron		Lead	
	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet
<u>Cow Creek east of Pittsburg</u>								
Sediment	42	28.3	13	8.7	27000	18171	21	14.1
Sediment	30	17.3	24	13.8	48600	27994	51	29.4
Crayfish	2.1	0.60	NA	NA	639	182	1.0	0.3
Largemouth Bass	0.72	0.19	NA	NA	93.2	24.4	ND	ND
Sunfish	1.4	0.34	NA	NA	163	40	0.5	0.1
<u>Spring River arm of Empire Lake</u>								
Sediment	24	13.1	22	12.0	17900	9738	160	87.0
Sediment	26	13.4	23	11.8	17900	9219	170	87.6
Insects	4.0	0.72	NA	NA	18.9	3.4	18	3.2
Crayfish	1.1	0.33	NA	NA	283	85	9.1	2.7
Common Carp	1.2	0.32	NA	NA	229	60	0.8	0.2
Channel Catfish	1.3	0.30	NA	NA	262	61	1.4	0.3
Crappie	1.2	0.29	NA	NA	98.1	23.5	0.9	0.2
Bluegill	0.82	0.20	NA	NA	62.3	15.2	1.0	0.2
<u>Shoal Creek arm of Empire Lake</u>								
Sediment	34	17.1	16	8.0	10300	5171	230	115.5
Sediment	33	17.0	15	7.7	10100	5202	230	118.5
Insects	2	0.45	NA	NA	832	188	20	4.5
Crayfish	3.1	0.91	NA	NA	345	101	8.9	2.6
Sunfish	1.1	0.27	NA	NA	106	26	7.3	1.8
Largemouth Bass	0.41	0.10	NA	NA	50.1	12.1	ND	ND
<u>Above the dam at Highway 166 just east of Baxter Springs</u>								
Sediment	24	15.84	16.0	10.6	18100	11946	220	145.2
Sediment	26	16.93	64.2	41.8	15700	10221	910	592.4
Insects	4.7	1.19	NA	NA	1040	263	2.8	0.7
Crayfish	7.3	1.71	NA	NA	1080	253	5.6	1.3
Common Carp	1.5	0.37	NA	NA	251	62	2.7	0.7
Common Carp	1.3	0.31	NA	NA	319	77	4.1	1.0
Flathead Catfish	0.98	0.19	NA	NA	144	29	ND	ND
<u>Below the dam at Highway 166 just east of Baxter Springs</u>								
Sediment	22	16.87	15.0	11.5	18600	14266	150	115
Sediment	21	15.23	24.0	17.4	24600	17835	310	225
Insects	12	3.20	NA	NA	8740	2334	15	4.0
Crayfish	4.4	1.18	NA	NA	4180	1120	12	3.2
Common Carp	0.9	0.20	NA	NA	194	43	1.4	0.3
Common Carp	0.52	0.12	NA	NA	137	31	2.7	0.6
White Bass	0.46	0.13	NA	NA	53.1	14.7	ND	ND

Table 6 (continued). Element concentrations in Cherokee County samples from ICP scans.

Sample	Element Concentration (mcg/g)							
	Magnesium		Manganese		Nickel		Strontium	
	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet
<u>Cow Creek east of Pittsburg</u>								
Sediment	2420	1629	997	671	26	17	45.2	30.4
Sediment	2430	1400	310	179	29	17	63.8	36.7
Crayfish	NA	NA	401	114	NA	NA	3.2	0.9
Largemouth Bass	NA	NA	15.2	4.0	NA	NA	0.67	0.2
Sunfish	NA	NA	53.2	13.0	NA	NA	0.92	0.2
<u>Spring River arm of Empire Lake</u>								
Sediment	2230	1213	268	146	25	14	30.7	16.7
Sediment	2240	1154	347	179	24	12	31.5	16.2
Insects	NA	NA	235	42	NA	NA	3.7	0.7
Crayfish	NA	NA	422	127	NA	NA	1.0	0.3
Common Carp	NA	NA	115.1	30	NA	NA	1.0	0.3
Channel Catfish	NA	NA	58.4	13.5	NA	NA	0.76	0.2
Crappie	NA	NA	23.3	5.6	NA	NA	1.2	0.3
Bluegill	NA	NA	79.7	19.4	NA	NA	0.8	0.2
<u>Shoal Creek arm of Empire Lake</u>								
Sediment	1670	838	378	190	43	22	11.8	5.9
Sediment	1680	865	367	189	43	22	11.9	6.1
Insects	NA	NA	314	71	NA	NA	6.3	1.4
Crayfish	NA	NA	208	61	NA	NA	4.1	1.2
Sunfish	NA	NA	32.6	8.1	NA	NA	0.87	0.2
Largemouth Bass	NA	NA	5.95	1.44	NA	NA	0.4	0.1
<u>Above the dam at Highway 166 just east of Baxter Springs</u>								
Sediment	2290	1511	359	237	25	17	32.6	21.5
Sediment	2430	1582	104	68	24	16	34.1	22.2
Insects	NA	NA	304	77	NA	NA	4.7	1.2
Crayfish	NA	NA	478	112	NA	NA	6.9	1.6
Common Carp	NA	NA	16.5	4.1	NA	NA	0.94	0.2
Common Carp	NA	NA	14.9	3.6	NA	NA	0.9	0.2
Flathead Catfish	NA	NA	6.77	1.34	NA	NA	1.3	0.3
<u>Below the dam at Highway 166 just east of Baxter Springs</u>								
Sediment	2000	1534	599	459	17	13	27.1	20.8
Sediment	2380	1726	694	503	27	20	33.0	23.9
Insects	NA	NA	1140	304	NA	NA	13.0	3.0
Crayfish	NA	NA	693	186	NA	NA	4.8	1.3
Common Carp	NA	NA	17.5	3.9	NA	NA	0.57	0.1
Common Carp	NA	NA	13.6	3.1	NA	NA	0.3	0.1
White Bass	NA	NA	11.6	3.2	NA	NA	0.3	0.1

Table 6 (concluded). Element concentrations in Cherokee County samples from ICP scans.

Sample	Element Concentration (mcg/g)			
	Vanadium		Zinc	
	Dry	Wet	Dry	Wet
<u>Cow Creek east of Pittsburg</u>				
Sediment	55.6	37.4	156	105
Sediment	57.1	32.9	261	150
Crayfish	NA	NA	80.7	23.0
Largemouth Bass	NA	NA	60.1	15.7
Sunfish	NA	NA	85.6	21.0
<u>Spring River arm of Empire Lake</u>				
Sediment	41.9	22.8	3580	1948
Sediment	42.9	22.1	3580	1844
Insects	NA	NA	556	100
Crayfish	NA	NA	144	43
Common Carp	NA	NA	287	75
Channel Catfish	NA	NA	111	26
Crappie	NA	NA	88.2	21.2
Bluegill	NA	NA	122	30
<u>Shoal Creek arm of Empire Lake</u>				
Sediment	16.0	8.0	3290	1652
Sediment	16.0	8.2	3310	1705
Insects	NA	NA	493	111
Crayfish	NA	NA	189	56
Sunfish	NA	NA	203	50
Largemouth Bass	NA	NA	75.6	18.3
<u>Above the dam at Highway 166 just east of Baxter Springs</u>				
Sediment	49.6	32.7	3040	2006
Sediment	50.5	32.9	11100	7226
Insects	NA	NA	310	78
Crayfish	NA	NA	224	52
Common Carp	NA	NA	286	71
Common Carp	NA	NA	502	120
Flathead Catfish	NA	NA	59.1	11.7
<u>Below the dam at Highway 166 just east of Baxter Springs</u>				
Sediment	35.8	27.5	2180	1672
Sediment	48.4	35.1	3460	2509
Insects	NA	NA	448	120
Crayfish	NA	NA	205	55
Common Carp	NA	NA	420	93
Common Carp	NA	NA	383	87
White Bass	NA	NA	68.2	18.8

1978). However, there are limited published data for whole body concentrations of aluminum in fish (e.g. Brumbaugh and Kane 1985, Guthrie and Cherry 1979, Wells et al. 1988). Berg and Burns (1985) and Brumbaugh and Kane (1985) reported differences in aluminum concentrations in different tissues.

Many of the aluminum concentrations in fish samples collected for this study were comparable to the values reported by Brumbaugh and Kane (1985) for smallmouth bass (*Micropterus dolomieu*), by Guthrie and Cherry (1979) for mosquitofish (*Gambusia affinis*), and by Wells et al. (1988) in Texas. However, the channel catfish and common carp samples from the Spring River arm of Empire Lake and the common carp from above the dam at Baxter Springs had relatively high aluminum concentrations. Brumbaugh and Kane (1985) showed that aluminum concentrations in gut contents of fish add much variability to whole body aluminum analyses and produced large differences in the concentrations measured. Analyses of additional samples with greater analytical precision would be required to determine if the high aluminum concentrations in fish from the Spring River arm of Empire Lake and from the Spring River upstream of the dam at Baxter Springs are the norms for those locations. In addition, because of the high variability introduced by gut content concentrations, separate analyses of gut contents and whole bodies should be considered.

#### Barium

In this study, barium was analyzed only in sediment samples. All barium concentrations were at the low end of the ranges of values reported for the continental U.S. by Shacklette and Boerngen (1984), for the northern Great Plains by Severson and Tidball (1979), and in western U.S. irrigation drainage study areas (Severson et al. 1987).

#### Beryllium

There is little information in the published literature about beryllium concentrations in biota. Beryllium has low solubility in water, and a low bioaccumulative tendency (Phillips and Russo 1978).

The low concentrations in all samples we collected are comparable to the concentrations found in several U. S. Department of the Interior studies in the western U.S. (Knapton et al. 1988, Lambing et al. 1988, Peterson et al. 1988, Radtke et al. 1988, Stephens et al. 1988). Beryllium concentrations in the areas we sampled should not be of concern.

### Boron

Boron is a naturally occurring trace element, essential for the growth and development of higher plants but not required by fungi or animals (Eisler 1990). Boron is generally found in concentrations that have little effect on animals. However, boron has been shown to cause severe reductions in mallard reproductive success (Smith and Anders 1989), was found in concentrations high enough to affect avian reproduction in agricultural drain water supplied to Kesterson National Wildlife Refuge (Hothem and Ohlendorf 1989), and is of concern in other agricultural drainwaters in the western U.S. (Smith and Anders 1989, Eisler 1990). Boron alone, and in concert with other trace elements, also has been shown to adversely affect chinook and coho salmon fry (Hamilton and Buhl 1990).

In this study, boron was analyzed only in sediment samples. The arithmetic mean boron concentration in soils of the U.S. reported by Shacklette and Boerngen (1984) was 33 mcg/g. Severson and Tidball (1979) reported a geometric mean of 41 mcg/g in the northern Great Plains. Severson *et al.* (1987) found a wide range of boron concentrations in sediments of nine Department of the Interior drainwater study areas in the western United States, from 0.6 to 210 mcg/g dry weight. All concentrations in Spring River and Cow Creek sediments were less than 10 mcg/g dry weight. We believe that these values are within background norms.

### Cadmium

Cadmium is a biologically nonessential teratogen, carcinogen, and probable mutagen. Freshwater biota are very sensitive to cadmium, with concentrations of 0.8 to 9.9 mcg/l known to be lethal to insects, crustaceans, or teleosts (Eisler 1985b). Many researchers have suggested that uptake through the gills is the common source of cadmium contamination in fish, but Dallinger and Kautzky (1985) and Klaverkamp *et al.* (1983) suggested that supply through food may be a more important source of cadmium (and other metal) contamination for rainbow trout than gill uptake. Cadmium has a low tendency to bioaccumulate, according to Phillips and Russo (1978), but other researchers have found high concentrations in aquatic invertebrates relative to water levels (Spehar *et al.* 1978). Studies have indicated that the majority of cadmium ingested by invertebrates is later egested (Benayoun *et al.* 1974, Boothe and Knauer 1972, Brown 1986, Martin *et al.* 1990, Timmermans and Walker 1989, VanDuyn-Henderson and Lasenby 1986).

Cadmium occurs with zinc in nature, and often is recovered as a product of zinc smelting. Smelters in Palmerton, Pennsylvania has been shown to be the center of considerable cadmium, zinc, and lead contamination (Beyer 1988, Beyer *et al.* 1985, Sileo and Beyer 1985).

Cadmium usually is present in water as a result of discharges from human activities (Eisler 1985, Pratrapp *et al.* 1989). Its subsequent availability to aquatic biota apparently is dependent on a variety of physical conditions (Kent and Johnson 1979, Pita and Hyne 1975, Wiener and Giesy, 1979.) Cadmium availability to biota differs little between hard water and soft water conditions (Wiener and Giesy 1979). Lodenius and Autio (1989) and Wiener and Giesy (1979) found that cadmium is more available at low Ph levels.

In sediments, Martin and Hartman (1984) found a mean dry weight cadmium concentration of 0.52 mcg/g in pothole wetlands in the north-central U.S., and a mean of 0.26 mcg/g in riverine wetlands. All concentrations were less than 1 mcg/g. Sediments from Lake Washington and Sardis Reservoir in Mississippi contained a mean of 0.36 mcg/g wet weight (Price and Knight 1978). Cadmium concentrations in the sediment samples from Cow Creek were not high, but all other sediment samples clearly were contaminated with cadmium.

Documentation of cadmium body burdens in wildlife and fish and effects of long-term exposure are lacking. According to Eisler (1985b), 5.0 ppm fresh (wet) weight should be considered life-threatening in whole animals.

Cadmium concentrations in whole fish from Department of the Interior studies in the western United States were very low (Knapton *et al.* 1988, Lambing *et al.* 1988, Peterson *et al.* 1988, Radtke *et al.* 1988, Schroeder *et al.* 1988, Stephens *et al.* 1988, Wells *et al.* 1988). Maximum whole body wet weight concentrations in fish collected for the NCBP were 1.04 mcg/g in 1976-1977, 0.41 mcg/g in 1978-1979, 0.35 mcg/g in 1980-1981, and 0.22 mcg/g in 1984. The comparable geometric means and 85th percentile values were 0.07 and 0.11, 0.04 and 0.09, 0.03 and 0.06, and 0.03 and 0.05 (Lowe *et al.* 1985, May and McKinney 1981, Schmitt and Brumbaugh 1990, Walsh *et al.* 1977).

Cadmium concentrations in aquatic insects, crayfish, and fish from the Spring River drainage all were less than 1 mcg/g wet weight. Although cadmium concentrations in Empire Lake and Spring River sediments were high, our samples indicate that the cadmium is not accumulated by biota of the lake or the river. However, we conclude that the high sediment concentrations mean that continued monitoring of cadmium in biota of the river is warranted.

### Chromium

Relatively little is known about effects of environmental chromium on animals, but at high ambient levels chromium is a mutagen, a teratogen, and a carcinogen. The chemistry of chromium in aquatic settings is not well understood, and can be modified by a variety of



environmental factors. Chromium is a trace nutrient for some animals, but its requirement in fish has not been established.

Chromium is not known to be biomagnified in food webs, and concentrations are usually greatest in the lowest trophic levels (Eisler 1986a). Knoll and Fromm (1960) indicated that  $\text{Cr}^{6+}$  is not accumulated in significant amounts by fish exposed to 2.5 mg/l. Phillips and Russo (1978) stated that chromium has a low bioaccumulation tendency. Hamilton and Reash (1988) believed that bone development of creek chubs (*Semotilus atromaculatus*) was affected by high concentrations of chromium and zinc in two streams in Ohio. A whole body chromium concentration of 4.0 mcg/g dry weight or more was considered by Eisler (1986a) to be evidence of chromium contamination. However, according to Buhler et al. (1977), Giesy and Wiener (1977), and Tong et al. (1974), fish usually contain less than 0.4 mcg/g dry weight.

The geometric mean dry weight chromium concentration in U.S. soils was 37 mcg/g; in the western U.S. the mean was 41 and in the east the mean was 33 mcg/g (Shacklette and Boerngen 1984). Means from western U.S. Department of the Interior drainwater studies were from 20 to 210 mcg/g (Severson et al. 1987). Chromium concentrations in sediments we sampled were not high.

Chromium concentrations in whole fish from Department of the Interior studies in the western U.S. were variable. Common carp from the lower Colorado River contained up to 1.9 mcg/g wet weight (Radtke et al. 1988). Most species from the study of the Lower Rio Grande and Laguna Atascosa National Wildlife Refuge (NWR) (Wells et al. 1988) contained 1.1 mcg/g or less, wet weight. *Tilapia* spp., however, contained 3.4 mcg/g wet weight, or 14 mcg/g dry weight. A sample of forage fish from Benton Lake NWR in Montana contained 17 mcg/g, and yellow perch (*Perca flavescens*) from the Sun River Irrigation Project contained 14 mcg/g dry weight (Knapton et al. 1988). White sucker (*Catostomus commersoni*) from Nelson Reservoir in northeastern Montana contained 17 mcg/g dry weight (Lambing et al. 1988). Common carp from a reservoir in central Wyoming contained 16 mcg/g dry weight, and fathead minnows (*Pimephales promelas*) from the same site contained 14 mcg/g dry weight (Peterson et al. 1988). Whole body chromium concentrations in fish from the southern San Joaquin valley in California ranged from 1.8 to 8.4 mcg/g dry weight (Schroeder et al. 1988).

Most biota samples collected for this study had chromium concentrations below Eisler's (1986a) 4.0 mcg/g dry weight concern level. However, the insects collected in the Spring River arm of Empire lake contained 4.0 mcg/g dry weight, insects and crayfish from above the dam at Baxter Springs, and insects from below the dam contained levels of concern. Chromium concentrations in biota of the Spring River should be monitored.

## Copper

Copper is a minor nutrient for plants and animals. In unpolluted waters it is usually found at concentrations less than 1 mg/l. Copper availability depends on water hardness in many settings (Hodson 1988). Hill (1977) did not consider copper toxicosis a serious threat to terrestrial organisms because copper is handled well by the liver and is seldom encountered in problematic concentrations. Copper concentrations in fish usually are homeostatically controlled (Cross *et al.* 1973, Giesy and Wiener 1977, Goodyear and Boyd 1972, Wiener and Giesy 1979). However, there are numerous documented cases of deleterious effects of copper in aquatic and terrestrial organisms, usually due to anthropogenic activities (e.g. Chupp and Dalke 1964, Clausen and Wolstrup 1978, Imlay and Winger 1983, McKim and Benoit 1971, Sprague *et al.* 1965).

In the western U.S. the arithmetic mean copper concentration in soils was 21 mcg/g; in the east the mean was 13 mcg/g (Shacklette and Boerngen 1984). Copper concentrations in sediments of western U.S. drainwater study areas ranged from 10 to 110 mcg/g (Severson *et al.* 1987). In this study, only sediments were analyzed for copper. One sediment sample from below the dam at Baxter Springs contained a markedly larger copper concentration than all other samples, but the concentration was smaller than those from many parts of the U.S.

## Iron

Iron is necessary for metabolic processes and especially for hemoglobin in fish, and can be expected to be found in higher concentrations than most other elements. Iron also has a high tendency to bioaccumulate, but large doses may cause serious problems. Fish accumulate large concentrations in the gills, but concentrations do not appear to change with age (Phillips and Russo 1978).

Iron is a major element in the earth's crust, and was present at concentrations of more than 10% in U.S. soils (Shacklette and Boerngen 1984). In western U.S. drainwater study areas Severson *et al.* (1987) found iron at concentrations of 1.6 to 6.1%. Sediment concentrations in the Spring River and Cow Creek were comparable to other U.S. locations.

In whole fish, Radtke *et al.* (1988) and Schroeder *et al.* (1988) found relatively consistent iron concentrations between sampling locations, whereas Peterson *et al.* (1988), Stephens *et al.* (1988), and Wells *et al.* (1988) found greater variation in their samples. These results suggest that iron concentrations may differ both between locations and between species. Iron concentrations in biota from the Spring River do not appear to warrant concern.

## Lead

Lead is biologically nonessential, and has long been recognized as a cumulative poison. The chemistry of lead introduced into aquatic systems is complex, and its availability to aquatic organisms varies (Eisler 1988b). Much lead entering fresh waters is precipitated, but decreasing Ph increases lead availability. The toxicity and bioconcentration of lead in aquatic organisms are increased by methylation (Hodson 1988, Phillips and Russo 1978). However, unmethylated lead has a low tendency to bioaccumulate (Phillips and Russo 1978). Lead poisoning in birds has been especially well studied, and effects in aquatic systems also have been well documented in many areas (Demayo et al. 1982, Wong et al. 1978).

Normally, little or no lead is available to aquatic systems. However, lead has been demonstrated to be at high levels in areas of metal mining (Benson et al. 1976, Chupp et al. 1964, Czarnecki 1985, Dwyer et al. 1988, Harwood et al. 1987, Knowlton et al. 1983, Niethammer et al. 1985, Roberts and Johnson 1978, Schmitt and Finger 1987) and metal smelting (Beyer 1988, Beyer et al. 1985, Dmowski and Karolewski 1979, Johnson et al. 1978). Wiener and Giesy (1979) found that lead was less available to aquatic biota in soft water systems. Much evidence suggests that often lead is not bioconcentrated (Eisler 1988b, Wong et al. 1978).

Lead in soils of the United States averaged 16 mcg/g (Shacklette and Boerngen 1984). Sediments "now constitute the largest global reservoir of..." lead (Eisler 1988b). Sediments in four relatively pristine pothole wetlands of the north-central U.S. had a geometric mean of 13 mcg/g dry weight (range 7.4-22). The mean for sediments from six national wildlife refuges in riverine settings was 6.6 mcg/g (range 1.1-14) (Martin and Hartman 1984). Pita and Hyne (1975) found less variation and lower concentrations of lead in sediments of reservoirs downstream from the tri-state mining area than they found in zinc and cadmium. Mean concentrations in two reservoirs were less than 25 mcg/g, but three other reservoirs averaged 36, 55, and 46 mcg/g. As could be expected in an area of past lead mining, sediments from the four downstream locations we sampled had accumulations of lead. Concentrations in Cow Creek were normal, but downstream concentrations were much higher.

Data on background lead concentrations in aquatic invertebrates appear to be limited. Soft tissues of *Physa* and *Gyraulus* snails from a pond on the Oklahoma State University campus contained 8.7 and 1.3 mcg/g mean dry weight concentrations, respectively. The shells had mean concentrations of 46.2 and 17.0 mcg/g (Namminga et al. 1974). Clams from Lake Washington and Sardis Reservoir in Mississippi had a mean lead concentration of 11.6 mcg/g wet weight. Plankton from the two lakes contained a mean of 501.6 mcg/g (Price and Knight 1978). Samples of the

Unionid clam *Anodonta grandis* from Lake Winnipeg contained less than 4 to over 150 ( $\bar{x}=97.8$ ) mcg/g. Lead concentrations were negatively correlated with shell weight (larger animals had lower body burdens) (Pip 1990).

Most lead concentrations in fish collected for Department of the Interior studies in the western United States were no higher than we found in Missouri River fish (Knapton et al. 1988, Lambing et al. 1988, Schroeder et al. 1988, Radtke et al. 1988, Peterson et al. 1988, Stephens et al. 1988., Wells et al. 1988). However, one brown trout sample from the Sun River project in Montana contained 4.1 mcg/g dry weight (Knapton et al. 1988).

In freshwater fish in the United States, geometric mean lead concentrations were 0.28 mcg/g wet weight in 1976-1977, 0.19 mcg/g in 1978-1979, 0.17 mcg/g in 1980-1981, and 0.11 mcg/g in 1984 (Lowe et al. 1985, May and McKinney 1981, Schmitt and Brumbaugh 1990, Walsh et al. 1977). This is a significant decline ( $P \leq 0.01$ ), and appears to represent a drop in environmental lead levels (Schmitt and Brumbaugh (1990). Corresponding 85th percentile values and maximum lead concentrations were 0.44 mcg/g and 4.93 mcg/g in 1976-1977, 0.32 mcg/g 6.73 mcg/g in 1978-1979, 0.25 mcg/g and 1.94 mcg/g in 1980-1981 (with the station normally having the highest concentrations not reporting), and 0.22 mcg/g and 4.88 mcg/g in 1984.

Our sampling indicates that there is no biomagnification of lead in biota of the Spring River under prevailing conditions. However, lead concentrations in virtually all biota samples were elevated. All invertebrate composites had elevated lead concentrations. All crayfish from Empire Lake and from the Spring River contained lead concentrations that concern us. Most lead concentrations in fish from Cow Creek and from the Spring River arm of Empire Lake were above the 85th percentile values from the NCBP. The concentration in the sunfish composite from the Shoal Creek arm of Empire Lake was well above the NCBP 85th percentile values, and concentrations in most other fish composites clearly indicate lead contamination. The impacts of the lead on fish and wildlife populations are unknown.

### Magnesium

Only sediments from this study were analyzed for magnesium. Magnesium is a common element in soils, and is found across the U.S. at a mean geometric concentration of 0.44% (Shacklette and Boerngen (1984). Concentrations in sediment samples we collected were low.

## Manganese

The geometric mean for manganese in U.S. soils is 330 mcg/g dry weight (Shacklette and Boerngen 1984). In western U.S. drainwater study areas, Severson *et al.* 1987) found concentrations from 200 to 3000 mcg/g. Concentrations in Cow Creek and Spring River sediments were comparable.

Phillips and Russo (1978) believed that manganese is "a relatively non-hazardous element in most waters due to the low toxicity of manganese to humans and to aquatic life and the insolubility of manganese under most natural conditions. We have very little information on normal concentrations of manganese in biota. Tevesz *et al.* (1989) and Hinch and Stephenson (1987) concluded that trace metal levels in bivalves "may not reflect environmental levels" because of differences in physiology and metal availability during periods of growth. With the exception of the aquatic insect sample from below the diversion dam at Baxter Springs, manganese concentrations in invertebrate samples we collected were within the 235-695 mcg/g range.

Manganese levels in fish are apparently well regulated under most conditions (Cross *et al.* 1973, Giesy and Wiener 1977, Goodyear and Boyd 1972, Wiener and Giesy 1979), and manganese has a low bioaccumulative tendency (Phillips and Russo 1978). Largemouth bass from ponds in South Carolina and from the Oklawaha River and a canal in Florida had mean whole body dry weight concentrations of 4.0 to 6.8 mcg/g (Goodyear and Boyd 1972). Manganese concentrations in the sunfish composite from Cow Creek and in the channel catfish and bluegill composites from the Spring River arm of Empire Lake were high compared to values in fish collected in the western United States (Knaption *et al.* 1988, Lambing *et al.* 1988, Schroeder *et al.* 1988, Radtke *et al.* 1988, Peterson *et al.* 1988, Stephens *et al.* 1988., Wells *et al.* 1988).

## Nickel

Nickel concentrations in many locations have been greatly altered as a result of mining and smelting operations, many industrial processes, and fossil fuel combustion. However, nickel has been considered less problematic than many other heavy metals. Nickel was considered by Phillips and Russo (1978) to have a low bioaccumulative tendency. However, it is bioaccumulated by at least some fish species (Tjalve *et al.* 1988).

Only sediment samples from this study were analyzed for nickel. The geometric mean for U.S. soils was 13 mcg/g; concentrations up to 700 mcg/g were found (Shacklette and Boerngen 1984). In soils analyzed for western U.S. drainwater studies, Severson *et al.* (1987) found nickel concentrations of 11 to 170 mcg/g. Soils from the northern Great Plains

contained 18 mcg/g (geometric mean) (Severson and Tidball (1979). Nickel concentrations in sediments we sampled were not high.

### Strontium

Levels of strontium in sediments and biota worldwide were altered after the 1940s by nuclear testing. In animals, strontium is incorporated into bone in place of calcium. Non-radioactive strontium has very low toxicity to aquatic animals and man, but radioactive strontium is extremely toxic (Phillips and Russo 1978). Beddington *et al.* (1989) studied strontium-90 concentrations in fish of Lake Windermere in England, and concluded that there likely has been long-term accumulation of strontium in sediments and biota. Strontium apparently was continuously remobilized and recycled.

In the U.S., strontium had a geometric mean concentration of 120 mcg/g in U.S. soils; 200 mcg/g in the west, 53 mcg/g in the east (Shacklette and Boerngen 1984). Northern Great Plains soils had a geometric mean concentration of 160 mcg/g (range 58-440 mcg/g) (Severson and Tidball 1979). Sediments of western U.S. drainwater study areas contained 170 to 920 mcg of strontium per gram (Severson *et al.* 1987). Compared to these values, the concentrations in Cow Creek and the Spring River in 1988 were low.

Strontium is "readily accumulated and retained by fish from either their food or water" (Phillips and Russo 1978). However, readily available calcium will limit strontium uptake. We have no standard against which to compare strontium concentrations in Cow Creek/Spring River biota, nor do we know if any of the strontium found was radioactive. Additional information about water characteristics in Cow Creek and the Spring River would aid an assessment of the importance of strontium concentrations that we found.

### Vanadium

Vanadium is an essential nutrient for at least some animals, but at high enough levels it is toxic (White and Dieter 1978). In our study, only vanadium concentrations in sediments were analyzed. The geometric mean vanadium concentration in U.S. soils, according to Shacklette and Boerngen (1984) is 58 mcg/g. Severson and Tidball (1979) found a mean of 54 mcg/g (range 20 to 96) in northern Great Plains soils. Severson *et al.* found concentrations of 36 to 210 mcg/g in sediments of western U.S. drainwater study areas. Based on comparisons to those values, concentrations in sediments we sample were not elevated.

## Zinc

Zinc is a required trace element for most organisms, but it is toxic at high concentrations (Holcombe et al. 1979, Taylor et al. 1982), and in some instances at relatively low concentrations (Bengtsson 1974). Zinc is a relatively mobile metal in natural settings, but zinc concentrations in many locations have been greatly increased by human activities (e.g. Beyer et al. 1985, Johnson et al. 1978, Niethammer et al. 1985, Roch et al. 1985, Sileo and Beyer 1985, Taylor et al. 1982). Zinc availability and toxicity are affected by many factors, especially Ph, water hardness, dissolved oxygen, and temperature (Phillips and Russo 1978, Skidmore 1964). Zinc is easily mobilized from soils (Taylor et al. 1982).

Zinc concentrations are well controlled metabolically in most organisms, and bioaccumulation or bioconcentration of zinc are highly dependent on location, feeding habits, and life stage of the organism being studied (Beyer et al. 1982, Beyer 1986, Giesy and Wiener 1977, Marshall et al. 1983, Murphy et al. 1978, O'Grady and Abdullah 1985, Roch et al. 1985, White and Cromartie 1985, Wiener and Giesy 1979). Zinc has a low bioaccumulative tendency, according to Phillips and Russo (1978), and Roch et al. (1985) demonstrated that zinc was not biomagnified in their aquatic Vancouver Island, British Columbia study area. Zinc and copper in water are synergistic at high concentrations, and affected rainbow trout (*Salmo gairdneri*) and immature Atlantic salmon (*Salmo salar*) more than simple additive effects of the two metals would suggest (Lloyd 1961, Sprague 1964). Concentrations and toxicity to fish may vary with migration or preparation for spawning (Fletcher et al. 1975, Fletcher and King 1978, O'Grady 1981), and with water chemistry and fish size (Bradley and Sprague 1985). Bone development of creek chubs in two streams in Ohio was thought to have been affected by high concentrations of chromium and zinc (Hamilton and Reash 1988).

Zinc concentrations in sediments we sampled reflect the effects of past mining in Cherokee and Crawford counties and along tributary streams in Missouri. In sediments from Cow Creek, zinc concentrations were well above the geometric means for the western and eastern U.S. (Shacklette and Boerngen 1984), the mean for soils of the northern Great Plains (Severson and Tidball 1979), and many of the values found in sediments of western U.S. drainwater study areas (Severson et al. 1987). Sediments from Empire Lake and from the Spring River were heavily zinc-laden. Seven of the eight samples had concentrations above the extremes found in other studies.

Namminga et al. (1974) found that soft tissues of *Physa* snails from a pond on the Oklahoma State University campus contained 86.9 mcg zinc per gram dry weight; soft tissues of *Gyraulus* snails contained 33.2 mcg/g. Giesy et al. (1980) found that the background zinc concentration in the crayfish *Procambarus acutus acutus* from an uncontaminated setting

in South Carolina was 86.5 mcg/g dry weight. Zinc concentrations in aquatic insects from Anderson Lake in the Coeur d'Alene River system (which was heavily affected by mining) decreased with distance from the lake inlet. Concentrations in chironomids ranged from 858 mcg/g at the inlet to 50 mcg/g in open water. Predaceous Libellulidae dragonfly nymphs contained 185 mcg/g at the inlet. Omnivorous *Chaoborus* nymphs contained 538 mcg/g in the open lake, and Helidae nymphs contained 188 mcg/g in the open lake (Rabe and Bauer 1977). Our sampling indicated that zinc levels in all aquatic invertebrate samples except those from Cow Creek were elevated. Giesy et al. (1980) reported that in water, *Procambarus acutus* accumulated zinc from water and did not reach a steady-state concentration. The concentration when exposed only to zinc in food reached a steady-state rapidly.

Maximum wet weight zinc concentrations in whole fish collected for the NCBP were 168.1 mcg/g in 1978-1979, 109.2 mcg/g in 1980-1981, and 118 mcg/g in 1984. Corresponding mean and 85th percentile concentrations were 23.8 and 46.3 mcg/g in 1978-1979, 21.4 and 40.1 mcg/g in 1980-1981, and 21.7 and 34.2 mcg/g in 1984 (Lowe et al. 1985, May and McKinney 1981, Schmitt and Brumbaugh 1990). Freshwater fish from the Savannah River contained 20.2 mcg/g wet weight or less (Winger et al. 1990). However, high zinc concentrations in whole fish were found in Department of the Interior studies in California (Schroeder et al. 1988), Texas (Wells et al. 1988), Utah (Stephens et al. 1988), Wyoming (Peterson et al. 1988), and Montana (Knapton et al. 1988). The zinc concentrations in all fish samples we collected were elevated relative to NCBP values. Concentrations in most fish samples from Empire Lake and from the Spring River were much more elevated than those in fish from Cow Creek. Concentrations in omnivorous fish were higher than concentrations in predators.

## CHLORINATED HYDROCARBON COMPOUNDS

Although use of organochlorine compounds has been severely restricted in the United States, chlorinated hydrocarbons were formerly widely used. Because of their persistence, they still are found in many biota. Results of chlorinated hydrocarbon analyses are shown in Table 7. The following organochlorine compounds were not detected in any sample: alpha BHC, beta BHC, gamma BHC, delta BHC, hexachlorobenzene, toxaphene, o,p'-DDD, endrin, o,p'-DDT, p,p'-DDT, and mirex.

### Chlordane Compounds

Chlordane is a complex mixture of compounds. Components of chlordane may include cis-chlordane, trans-chlordane, cis-nonachlor, trans-nonachlor, chlordanes, and heptachlor, as well as other compounds (Cardwell et al. 1977, National Research Council of Canada 1974).



Table 7. Chlorinated hydrocarbon concentrations  
in Cherokee County Samples.

Sample	Percent Moisture	Percent Lipid	Concentration (mcg/g wet weight)			
			cis- Chlordane	trans- Chlordane	cis- Nonachlor	trans- Nonachlor
<u>Cow Creek east of Pittsburg</u>						
Sediment	25.00	NA	ND	ND	ND	ND
Sediment	40.50	NA	ND	ND	ND	ND
Crayfish	73.00	4.97	ND	ND	ND	0.03
Sunfish	74.60	2.28	0.05	0.14	0.04	0.02
Largemouth Bass	74.00	4.06	0.16	0.07	0.04	0.17
<u>Spring River arm of Empire Lake</u>						
Sediment	36.50	NA	ND	ND	ND	ND
Sediment	38.00	NA	ND	ND	ND	ND
Insects	NA	2.46	ND	ND	ND	ND
Crayfish	NA	1.25	ND	ND	ND	ND
Common Carp	73.60	3.63	ND	ND	ND	0.01
Crappie	74.20	2.27	0.01	0.01	ND	0.01
Bluegill	73.80	2.52	0.01	ND	ND	0.03
Channel Catfish	76.00	5.30	0.01	0.01	ND	0.02
<u>Shoal Creek arm of Empire Lake</u>						
Sediment	45.50	NA	ND	ND	ND	ND
Sediment	39.50	NA	ND	ND	ND	ND
Insects	NA	2.50	ND	ND	ND	0.01
Crayfish	70.50	2.22	ND	ND	ND	ND
Sunfish	76.00	1.87	0.01	ND	ND	0.03
Largemouth Bass	75.80	2.52	0.01	ND	ND	0.02
<u>Above the dam at Highway 166 just east of Baxter Springs</u>						
Sediment	28.00	NA	ND	ND	ND	ND
Sediment	31.00	NA	ND	ND	ND	ND
Insects	66.00	3.15	ND	ND	ND	0.02
Crayfish	78.50	3.35	ND	ND	ND	ND
Common Carp	74.00	5.93	0.02	0.02	ND	0.02
Common Carp	76.80	2.11	0.02	0.01	ND	0.01
Flathead Catfish	80.00	2.74	0.02	0.01	ND	0.02
<u>Below the dam at Highway 166 just east of Baxter Springs</u>						
Sediment	21.50	NA	ND	ND	ND	ND
Sediment	26.50	NA	ND	ND	ND	ND
Insects	68.00	5.97	ND	ND	ND	ND
Crayfish	78.00	4.58	ND	ND	ND	ND
Common Carp	78.50	2.65	ND	ND	ND	ND
Common Carp	77.00	1.63	0.01	0.01	ND	0.02
White Bass	71.00	6.17	0.03	0.02	ND	0.04

Table 7 (continued). Chlorinated hydrocarbon concentrations in Cherokee County Samples.

Sample	Concentration (mcg/g wet weight)				
	Oxychlordane	Heptachlor Epoxide	Chlordane Total <sup>a</sup>	Dieldrin	Cyclodiene Total <sup>b</sup>
<u>Cow Creek east of Pittsburg</u>					
Sediment	ND	ND	ND	ND	ND
Sediment	ND	ND	ND	ND	ND
Crayfish	0.01	ND	0.04	ND	0.04
Sunfish	0.04	0.03	0.32	0.01	0.33
Largemouth Bass	0.06	0.07	0.57	0.03	0.60
<u>Spring River arm of Empire Lake</u>					
Sediment	ND	ND	ND	ND	ND
Sediment	ND	ND	ND	ND	ND
Insects	ND	ND	ND	0.01	0.01
Crayfish	ND	ND	ND	ND	ND
Common Carp	ND	ND	0.01	0.02	0.03
Crappie	ND	ND	0.03	0.01	0.04
Bluegill	0.01	0.01	0.06	0.02	0.08
Channel Catfish	ND	ND	0.04	0.01	0.05
<u>Shoal Creek arm of Empire Lake</u>					
Sediment	ND	ND	ND	ND	ND
Sediment	ND	ND	ND	ND	ND
Insects	ND	ND	0.01	ND	0.01
Crayfish	ND	ND	ND	ND	ND
Sunfish	0.01	ND	0.05	ND	0.05
Largemouth Bass	ND	ND	0.03	0.01	0.04
<u>Above the dam at Highway 166 just east of Baxter Springs</u>					
Sediment	ND	ND	ND	ND	ND
Sediment	ND	ND	ND	ND	ND
Insects	ND	ND	0.02	0.01	0.03
Crayfish	ND	ND	ND	ND	ND
Common Carp	ND	0.01	0.07	0.02	0.09
Common Carp	ND	0.01	0.05	0.01	0.06
Flathead Catfish	0.01	0.01	0.07	0.01	0.08
<u>Below the dam at Highway 166 just east of Baxter Springs</u>					
Sediment	ND	ND	ND	ND	ND
Sediment	ND	ND	ND	ND	ND
Insects	ND	ND	ND	0.02	0.02
Crayfish	ND	ND	ND	ND	ND
Common Carp	ND	ND	ND	0.01	0.01
Common Carp	0.01	ND	0.05	ND	0.05
White Bass	0.02	0.04	0.15	0.04	0.19

<sup>a</sup> All chlordane compounds and metabolites.

<sup>b</sup> chlordane/heptachlor compounds, aldrin, and dieldrin.

Table 7 (concluded). Chlorinated hydrocarbon concentrations in Cherokee County Samples.

Sample	Concentration (mcg/g wet weight)			
	o,p'-DDE	p, p'-DDE	p,p'-DDD	total PCBs
<u>Cow Creek east of Pittsburg</u>				
Sediment	ND	ND	ND	ND
Sediment	ND	ND	ND	ND
Crayfish	ND	0.01	ND	0.17
Sunfish	ND	0.03	0.03	0.72
Largemouth Bass	ND	0.04	0.05	1.10
<u>Spring River arm of Empire Lake</u>				
Sediment	ND	ND	ND	ND
Sediment	ND	ND	ND	ND
Insects	ND	ND	ND	ND
Crayfish	ND	ND	ND	ND
Common Carp	ND	0.02	ND	0.42
Crappie	ND	0.01	ND	0.24
Bluegill	ND	0.03	ND	0.50
Channel Catfish	ND	0.03	ND	0.63
<u>Shoal Creek arm of Empire Lake</u>				
Sediment	ND	ND	ND	ND
Sediment	ND	ND	ND	ND
Insects	ND	0.01	ND	ND
Crayfish	ND	ND	ND	ND
Sunfish	ND	0.01	ND	0.15
Largemouth Bass	ND	0.02	ND	0.26
<u>Above the dam at Highway 166 just east of Baxter Springs</u>				
Sediment	ND	ND	ND	ND
Sediment	ND	ND	ND	ND
Insects	ND	0.01	ND	ND
Crayfish	ND	ND	ND	ND
Common Carp	ND	0.01	ND	0.13
Common Carp	ND	0.01	ND	0.13
Flathead Catfish	ND	0.02	ND	0.48
<u>Below the dam at Highway 166 just east of Baxter Springs</u>				
Sediment	ND	ND	ND	ND
Sediment	ND	ND	ND	ND
Insects	ND	ND	ND	ND
Crayfish	ND	ND	ND	ND
Common Carp	ND	0.01	ND	0.20
Common Carp	ND	0.03	0.02	0.51
White Bass	0.03	0.04	ND	ND

Oxychlordanes is a metabolite of chlordane components. Cis- and trans-nonachlor and cis-chlordane are more readily stored than are other chlordane components (Cardwell *et al.* 1977, Winger *et al.* 1984).

Chlordane formerly was used for control of a variety of soil insects, including termites and agricultural pests. It is now used less for agricultural pests, and Arruda *et al.* (1987) suggested that the main sources of chlordane contamination of aquatic systems are urban areas. Chlordane is very persistent and highly toxic to aquatic organisms and birds. Detrimental effects of chlordane components or metabolites on birds have been demonstrated by Blus *et al.* (1983) and Stickel *et al.* (1979, 1983). Heptachlor has been used for controlling insects in seeds and for control of fire ants. It is also a constituent of chlordane, so it is difficult to separate the sources of heptachlor and heptachlor epoxide, a more toxic metabolite of heptachlor (Schmitt *et al.* 1990). Heptachlor has been demonstrated to be long-lasting (Beyer and Krynitsky 1989, Gish and Hughes 1982) and to have detrimental effects on birds (Blus *et al.* 1984, 1985, Ferguson 1964, Henny *et al.* 1983, 1984, Rosene 1965, Stickel *et al.* 1965, Wright 1965) and mammals (Clark *et al.* 1980, Clawson and Clark 1989, Rosene 1965).

In whole carp from Tuttle Creek Reservoir, Kansas, Arruda *et al.* (1988) found chlordane in all eight composites analyzed and heptachlor in seven of the eight composites. Chlordane was detected at higher concentrations than other contaminants; the mean concentration was 0.1 mcg/g wet(?) weight, the maximum was 0.17 mcg/g.

Chlordane compounds were not detected in fish from the Lower Rio Grande Valley (Wells *et al.* 1988), the lower Colorado River (Radtke *et al.* 1988), the Middle Green River basin in Utah (Stephens *et al.* 1988), the Kendrick project in central Wyoming (Peterson *et al.* 1988), the Milk River in Montana (Lambing *et al.* 1988), the Sun River in Montana (Knapton *et al.* 1988). However, Schroeder *et al.* (1988) found chlordane compounds in common carp from two of three locations sampled for the Tulare Lake Bed Area study in the San Joaquin Valley in California. Cis- and trans-chlordane and trans-nonachlor were found in carp composites from one location, in concentrations ranging from 0.01 to 0.05 mcg wet weight for each compound. Cis- and trans-chlordane in concentrations from 0.10 to 0.15 mcg/g wet were found in fish from another location.

The geometric mean heptachlor concentration in fish collected each year from 1970 through 1973 for the National Pesticide Monitoring Program (NPMP) was 0.01 mcg/g wet weight. In 1974 heptachlor was not detected in any sample. The maximum concentrations found each year were 0.40 mcg/g in 1970, 1.0 mcg/g in 1971, 0.23 mcg/g in 1972, and 0.05 mcg/g in 1973. Chlordane compound concentrations in fish collected for the NCBP from 1976 through 1984 were reported by Schmitt *et al.* (1983, 1985, 1990).

Nationwide, the decreasing concentrations of chlordane and the increasing proportions of trans-nonachlor, the most persistent component of chlordane, in fish collected for the NCBP indicate that the input of chlordane to aquatic systems in the U.S. may be declining. In general, the highest chlordane compound concentrations reported from the NCBP came from the midwest and from Hawaii (Schmitt *et al.* 1990).

The National Academy of Sciences and National Academy of Engineering [(NAS/NAE) 1973] recommended that to protect aquatic life, the whole body wet weight concentration of all cyclodiene compounds together should not exceed 0.1 mcg/g. No chlordane/heptachlor compounds were detected in 17 of the 33 samples we collected. However, the high total chlordane compound concentrations in the fish samples from Cow Creek suggest episodic exposure in the vicinity of Pittsburg, also the only site at which cis-nonachlor was detected. The differences in food habits between common carp and white bass may account for the differences in chlordane compound concentrations in the two species at the collection site below the dam at Baxter Springs. The relatively short life span of white bass indicates that the elevated concentration in the white bass sample occurred no more than a few years before our collections.

#### Aldrin and Dieldrin

Aldrin and dieldrin are insecticides once supplied in many formulations primarily for use on soil insects. In addition, dieldrin is the primary metabolite of aldrin in animals. Aldrin and/or dieldrin have been found to be detrimental to fish (Anderson and Fenderson 1970, Johnson and Finley 1980), birds (e.g. Hill 1982, Jones *et al.* 1978, Labisky and Lutz 1967, McEwen and Brown 1966, Newton and Bogan 1978, Wiemeyer *et al.* 1986), frogs (Mayer and Eilersieck 1986), snakes (Flickinger and King 1972), turtles (Flickinger and Mulhern 1980), and bats and other mammals (Blus 1978, Clark 1983, 1988, Clark *et al.* 1978, 1980, 1983, Clark and Prouty 1984).

Nationwide, geometric mean dieldrin concentrations in fish collected for the NPMP in the early 1970s were little different from the means from the NCBP in the late 1970s and early 1980s. Wet weight mean concentrations were 0.08 mcg/g in 1970, 0.07 mcg/g in 1971 and 1972, 0.05 mcg/g in 1973, and 0.09 mcg/g in 1974 (Schmitt *et al.* 1981). The geometric mean wet weight residues of dieldrin in fish did not change significantly from 1976 through 1984. They were 0.06 mcg/g in 1976-1977, 0.05 mcg/g in 1978-1979, and 0.04 mcg/g in 1980-1981 and 1984 (Schmitt *et al.* 1983, 1985, 1990).

Dieldrin was detected at very low concentrations in 15 of the 33 samples. The concentrations in invertebrates from the Spring River arm of Empire Lake and from Baxter Springs indicate relatively recent use.

### Total Cyclodiene Compounds

The three samples that exceeded the NAS/NAE cyclodiene compounds recommendation were the fish composites that were high in chlordane compounds. Dieldrin concentrations pose little concern in the areas we sampled, but long-term exposure to chlordane compounds in parts of the Spring River watershed appears likely.

### DDT Compounds

DDT and its metabolites are probably the most studied organochlorine contaminants. Although no longer approved for use, DDT compounds are very persistent. In addition, dicofol acaricide may be contaminated with DDT, and is a possible source of DDE (Hunt *et al.* 1986, Risebrough *et al.* 1985, Schmitt *et al.* 1985, White and Krynsky 1986). DDT compounds have been shown to have a variety of detrimental effects, especially reduced recruitment in birds (e.g. Blus *et al.* 1977, Henny and Herron 1989, Henny *et al.* 1984, Hickey and Anderson 1968, Longcore *et al.* 1971, Lundholm 1987, Newton and Bogan 1978, Ratcliffe 1967, Wiemeyer *et al.* 1986). Effects on fish, frogs, and bats also have been documented (e.g. Berlin *et al.* 1981, Burdick *et al.* 1964, Clark 1988, Geluso *et al.* 1976, Kirk 1988, Sanders 1970).

DDT is metabolized to DDE and DDD by most fish species, so the ratio of DDT to its metabolites usually is indicative of time elapsed since introduction (Aguilar 1984). In addition, the ratios of ortho-para (o,p') DDT and metabolites to the para-para (p,p') forms are indicative of the sources of contamination. The o,p'- compounds are shorter-lived than their p,p'- analogs, and technical grade DDT contains less than 20% of the o,p'- compound (Fry and Toone 1981, Schmitt *et al.* 1985, 1990). Therefore, high concentrations of the o,p'- forms of DDT or its metabolites indicate "relatively recent inputs and pollution sources other than insecticides - e.g., pesticide manufacturing and formulation sites or chemical waste dumps" (Schmitt *et al.* 1985).

In the north-central U.S., fish from National Wildlife Refuge wetlands sampled by Martin and Hartman (1985) contained lower organochlorine residues than fish from most other parts of the country. The maximum concentration found in their study was 0.51 mcg/g DDE wet weight in a Rio Grande chub (*Gila nigrescens*) sample from Monte Vista NWR in Colorado. Fish from Lake Poinsett, South Dakota in 1967-1968 contained low levels of DDT compounds. The maximum concentration detected in any sample was 0.21 mcg/g wet weight in channel catfish (Hannon *et al.* 1970). In Tuttle Creek Lake in 1970-1971, Klaassen and Kadoum (1975) found low total DDT concentrations in fish they analyzed. Although 98 percent of the fish samples analyzed contained DDT compounds, most total DDT concentrations were less than 0.10 mcg/g wet weight. The highest concentration observed was 0.57 mcg/g in a

freshwater drum sample. In the same lake in 1985, Arruda *et al.* (1988) found p,p'-DDE and p,p'-DDD in 15 of 16 common carp samples. However, mean concentrations were all less than 0.1 mcg/g wet weight.

In western U.S. Department of the Interior studies, DDT and DDT homolog concentrations were variable. Wells *et al.* (1988) found p,p'-DDE at up to 9.9 mcg/g wet weight in fish from the lower Rio Grande River. The median concentration, however, was 0.38 mcg/g. In the lower Colorado River drainage, common carp samples from a few locations contained less than 0.1 mcg/g p,p'-DDE wet weight, all but two samples contained less than 0.2 mcg/g (Radtke *et al.* 1988). The Tulare basin study in the San Joaquin valley in California (Schroeder *et al.* 1988) documented p,p'-DDD, -DDE, and -DDT in mosquitofish, common carp, and yellow bullhead. Geometric means ranged from below the detection limit in 1/3 of the samples to 0.32 mcg/g wet weight p,p'-DDE in mosquitofish from one location. In that study, the high ratios of DDT to DDE and DDD indicated recent inputs of DDT to the system. In Montana, individual DDT compound concentrations in whole fish were below 0.03 mcg/g wet weight (Knapton *et al.* 1988). In limited samples from Utah, DDT compounds were below the detection limits (Stephens *et al.* 1988).

Mean DDT compound concentrations in fish collected for the NPMP and the NCBP declined in the 1970s, but did not change during the early 1980s. However, concentrations of p,p'-DDT did decline, and apparent inputs into most aquatic systems have diminished (Schmitt *et al.* 1990). Nationwide wet weight geometric means for total DDT (p,p'- forms) from the NCBP were 6.54 mcg/g in 1976-1977, 10.62 mcg/g in 1978-1979, 6.50 mcg/g in 1980-1981, and 9.08 mcg/g in 1984 (Schmitt *et al.* 1983, 1985, 1990). Data from the NCBP support the indications in the papers above that, in general, DDT compound concentrations in the midwest are lower than those found in many other parts of the country.

DDT compounds were not detected in any of the sediment samples we collected, nor in most of the insect and crayfish samples. Even when detected, the concentrations were very low.

### PCBs

Polychlorinated biphenyls formerly were used in a variety of commercial applications. Although a ban on U.S. manufacture and processing of PCBs went into effect in the 1970s, the pool of sources of PCB compounds is large enough to assure continued introduction of PCBs into the environment (Eisler 1986b).

PCB compounds are some of the most ubiquitous environmental contaminants. They are very slow to degrade, and long range transport of PCBs has been well documented. They have been found in most environments throughout the world (e.g. Aguilar 1983, Bowes and Lewis

1974, Hidaka *et al.* 1983, Knap and Jickells 1983, Muir *et al.* 1988, Solbakken *et al.* 1984, Weber 1983). PCB compounds are relatively insoluble in water, but most are very soluble in biological lipids. In addition, PCBs are strongly adsorbed on aquatic sediments (Eisler 1986b). Therefore, although PCBs may be anaerobically degraded (Huckins *et al.* 1988, Rhee *et al.* 1989), benthic organisms are at special risk from PCBs (Dunnivant *et al.* 1989, Fry and Fisher 1990, Stainken 1984).

Effects of PCBs include a variety of maladies in many animals (e.g. Eisler 1986b, Hoffman *et al.* 1986, Hogan and Brauhn 1975, Koval *et al.* 1987, Linzey 1987, Mauch *et al.* 1978, Mayer *et al.* 1985, Newton and Bogan 1978, Stendell 1976, White and Cromartie 1977, Wren *et al.* 1987b). PCBs also may alter the effects of other contaminants (Bills *et al.* 1981, Wren *et al.* 1987a). PCBs are bioaccumulated and biomagnified in the environment, although which is more important has been debated (e.g. Crossland *et al.* 1987, Hunter *et al.* 1980, Macek *et al.* 1979, Thomann 1981). The bioconcentration factor for Aroclor<sup>R</sup> in freshwater invertebrates can be as high as 47,000 (Eisler 1986b). Food chain structure was found by Rasmussen *et al.* to play a great role in PCB levels in lakes in Ontario. In addition, impurities in PCBs such as polychlorinated dibenzo-furans may be extremely toxic.

The EPA criteria for protection of aquatic life (EPA 1980b) state that the whole body fresh weight concentration of PCBs should be less than 0.4 mcg/g. However, that criterion was based on protection of human health, based on research using striped bass. Whole body PCB concentrations of 0.4 mcg/g fresh weight were associated with reproductive toxicity in rainbow trout (EPA 1980b). The criterion probably should be lower for nonmigratory benthic species (Eisler 1986b).

In the north-central United States, Martin and Hartman (1985) found PCB concentrations in few of the whole fish samples that they analyzed. A mixed species sample from Alamosa NWR in Colorado contained 1.2 mcg/g wet weight, two samples from other locations contained less than 1 mcg/g, and 23 other samples from various refuges did not contain detectable PCB concentrations. In analysis of fish collected nationwide for the NPMP, total wet weight PCB concentrations ranged from below the detection limit to 75.0 mcg/g from 1970 through 1974 (Schmitt *et al.* 1981). Nationwide geometric means were 1.20, 1.03, 1.20, 0.78, and 0.95 mcg in 1970, 1971, 1972, 1973, and 1974, respectively. Separate PCBs were not analyzed before 1973, when the mean for Aroclor<sup>R</sup> 1254 was 0.58 mcg/g. In 1974 the nationwide mean was 0.82 mcg/g wet weight. Mean Aroclor<sup>R</sup> 1254 and total PCB concentrations were 0.47 and 0.87 mcg/g in 1976-1977, and 0.47 and 0.86 mcg/g in 1978-1979 (Schmitt *et al.* 1983). In 1980-1981, the values were 0.24 and 0.53 mcg/g (Schmitt *et al.* 1985). By 1984, the Aroclor<sup>R</sup> 1254 and total PCB mean concentrations nationwide had declined to 0.21 and 0.39 mcg/g wet weight, respectively.



The maximum nationwide values in 1984 were 4.0 mcg/g and 6.7 mcg/g. Since 1976, both Aroclor<sup>®</sup> 1254 and total PCB mean concentrations have shown highly significant declines (Schmitt *et al.* 1990).

With the exception of the crayfish sample from Cow Creek, PCBs were detected only in fish. The concentration in the Cow Creek crayfish sample was below the EPA criterion for protection of aquatic life. The PCB concentration in seven of the 15 fish composites exceeded the 1984 NCBP mean, but all concentrations were well below the maximum observed in the 1984 NCBP. The seven composites contained concentrations higher than the EPA protection criterion. The highest PCB concentrations were found in Cow Creek and the Spring River arm of Empire Lake.

#### ALIPHATIC HYDROCARBON COMPOUNDS

Aliphatic, naphthenic, and aromatic hydrocarbons of different molecular weights are present in varying amount in different crude and refined petroleum mixtures. Although wildlife and fish are commonly exposed to petroleum pollutants, assessments of petroleum hydrocarbon concentrations and their effects on wildlife are attempted infrequently, in part because the assessments often seem too difficult to make (Hall and Coon 1988). However, the effects of petroleum compounds on birds have been documented after oil spills, and effects on the survival of adults, eggs and young have been well studied (e.g. Albers 1980, Albers and Szaro 1978, Coon *et al.* 1979, Eastin and Hoffman 1979, Fleming *et al.* 1982, Hoffman 1979, Holmes *et al.* 1979, King and Lefever 1979, Miller *et al.* 1982, Patton and Dieter 1980, Szaro *et al.* 1978, 1980, Tarshis and Rattner 1982).

Aromatic hydrocarbons comprise 15 to 40% of refined oils (Korte and Boedefeld 1978), but are difficult to study because they are readily lost from aquatic systems. Lower molecular weight hydrocarbons are more quickly metabolized than are heavier compounds, both in fish and in microorganisms in the river (Hall and Coon 1988), and studies of the heavier-weight naphthenic and aliphatic components of crude and refined petroleum have been limited (Hellou *et al.* 1989). The sources of aromatic and aliphatic hydrocarbons in aquatic systems are generally considered to be combustion of fossil fuels, antifouling agents such as creosote, and spills or discharges (see Winger *et al.* 1990 and the citations therein).

Results of aliphatic hydrocarbon analyses are shown in Table 8. The aliphatic residues in fish suggest differences between species in uptake or metabolizing of aliphatics. Total aliphatic hydrocarbons exceeded the concentrations found in cutthroat trout (*Salmo clarki*) that were negatively affected by crude oil ( $\geq 4.63$  mcg/g wet(?) weight, Woodward *et al.* 1981) in three of the fish composites. Woodward *et al.*

(1983) studied effects of a petroleum refinery seepage on cutthroat trout, and found that body burdens associated with reduced fish health were 2.7 mcg/g for naphthalenes (which are aromatics), and 0.971 mcg/g for all aliphatics. Aromatics were the dominant compounds in the refinery seepage. Naphthalenes were most readily taken up by the trout.

The total of aliphatic compounds in the channel catfish composite from the Spring River arm of Empire Lake, the two common carp composites from above the dam at Baxter Springs, and the carp and white bass composites from below the dam was above the level at which Woodward *et al.* (1983) found discernible effects.

Because pristane and phytane are metabolized less readily than comparable straight-chain aliphatics, high ratios of n-C17 and n-C18 to pristane and phytane, respectively, indicate recent exposure to petroleum (Anderson *et al.* 1978, Farrington *et al.* 1973, Hall and Coon 1988). In crayfish, the n-C17 to pristane ratios at Cow Creek and at the Shoal Creek arm of Empire Lake suggest recent exposure (Table 8, Figure 2). However, n-C18 to phytane ratios were less conclusive (Table 8, Figure 3). In 10 of the 45 samples the n-C18/phytane ratio was less than 1, which suggests chronic exposure to petroleum contamination. Pristane was not detected in nine of the 14 fish composites, but the n-C17 ratios that could be calculated and the n-C17 concentrations in fish composites all indicated recent petroleum exposure. N-C18/phytane ratios in fish composites were more variable. Some indicated recent exposure, others indicated long-term contamination.

Aliphatic hydrocarbons with odd numbers of carbon atoms are attributable to living organisms (Blumer *et al.* 1972, Woodward *et al.* 1988, Veith *et al.* 1979), but some researchers have associated n-heptadecane with petroleum contamination. Aliphatic hydrocarbon concentrations in samples we collected indicated petroleum contamination, but the proportion of n-heptadecane relative to all other aliphatics suggests several possibilities: that n-C17 may be taken up by aquatic organisms in greater amounts than other aliphatics; depuration of n-C17 may be exceedingly slow; or there is a natural source of the compound in the river.

Table 8. Aliphatic hydrocarbon concentrations in Cherokee County Samples.

Sample	Concentration (mcg/g wet weight)					
	n-dodecane	n-tridecane	n-tetradecane	octylcyclo-hexane	n-pentadecane	nonylcyclo-hexane
<u>Cow Creek east of Pittsburg</u>						
Sediment	ND	ND	0.01	ND	0.01	ND
Sediment	0.04	0.05	0.05	0.02	0.06	0.03
Crayfish	ND	0.01	ND	ND	0.09	0.05
Sunfish	ND	ND	0.01	ND	0.03	ND
Largemouth Bass	0.05	0.06	0.02	ND	0.14	0.01
<u>Spring River Arm of Empire Lake</u>						
Sediment	ND	ND	ND	ND	0.02	ND
Sediment	ND	ND	0.01	ND	0.01	ND
Insects	0.04	0.06	0.05	ND	0.06	ND
Crayfish	0.54	0.52	0.11	0.12	0.05	0.08
Common Carp	ND	ND	0.01	ND	0.10	ND
Crappie	ND	ND	0.01	ND	0.04	ND
Bluegill	ND	ND	ND	ND	0.02	ND
Channel Catfish	ND	0.03	0.01	ND	0.24	ND
<u>Shoal Creek Arm of Empire Lake</u>						
Sediment	ND	ND	ND	ND	0.02	ND
Sediment	ND	ND	ND	ND	0.01	ND
Insects	0.01	0.02	0.02	ND	0.06	ND
Crayfish	ND	ND	ND	ND	0.02	ND
Sunfish	ND	ND	ND	ND	0.01	ND
Largemouth Bass	ND	ND	ND	ND	0.08	ND
<u>Above the dam at Highway 166 just east of Baxter Springs</u>						
Sediment	ND	ND	0.01	ND	0.01	ND
Sediment	ND	ND	ND	ND	ND	ND
Insects	0.04	0.05	0.04	ND	0.06	ND
Crayfish	ND	0.02	ND	ND	0.07	ND
Common Carp	ND	0.10	0.02	ND	0.10	ND
Common Carp	0.02	0.04	0.03	ND	0.12	ND
Flathead Catfish	ND	ND	0.01	ND	0.04	ND
<u>Below the dam at Highway 166 just east of Baxter Springs</u>						
Sediment	ND	0.01	0.03	ND	0.03	0.01
Sediment	ND	0.01	0.02	ND	0.02	ND
Insects	0.03	0.01	0.05	ND	0.03	ND
Crayfish	0.10	0.13	0.11	0.04	0.21	0.05
Common Carp	ND	ND	0.01	ND	0.25	ND
Common Carp	ND	ND	ND	ND	0.16	ND
White Bass	ND	0.07	0.01	ND	0.40	ND

Table 8 (concluded). Aliphatic hydrocarbon concentrations  
in Cherokee County Samples.

Sample	Concentration (mcg/g wet weight)					
	n-heptadecane	pristane	n-C17/ pristane	n-octadecane	phytane	n-c18/ phytane
<u>Cow Creek east of Pittsburg</u>						
Sediment	0.01	0.04	0.25	0.01	ND	NA
Sediment	0.08	0.22	0.36	0.07	0.05	1.40
Crayfish	0.16	0.07	2.29	0.03	0.10	0.30
Sunfish	0.02	0.01	2.00	0.02	0.02	1.00
Largemouth Bass	0.37	0.04	9.25	0.03	0.05	0.60
<u>Spring River Arm of Empire Lake</u>						
Sediment	0.06	0.04	1.50	0.02	0.03	0.67
Sediment	0.07	0.04	1.75	0.02	0.03	0.67
Insects	0.24	0.06	4.00	0.12	0.07	1.71
Crayfish	0.08	0.09	0.89	0.18	0.04	4.50
Common Carp	5.60	0.02	280.00	0.38	0.11	3.45
Crappie	0.50	ND	NA	0.02	0.03	0.67
Bluegill	0.69	ND	NA	0.03	0.02	1.50
Channel Catfish	1.90	ND	NA	0.04	0.07	0.57
<u>Shoal Creek Arm of Empire Lake</u>						
Sediment	0.08	0.02	4.00	0.02	0.02	1.00
Sediment	0.09	0.02	4.50	0.02	0.02	1.00
Insects	0.32	0.02	16.00	0.04	0.01	4.00
Crayfish	0.17	0.05	3.40	0.02	0.07	0.29
Sunfish	0.02	ND	NA	ND	0.02	NA
Largemouth Bass	0.67	ND	NA	0.01	ND	NA
<u>Above the dam at Highway 166 just east of Baxter Springs</u>						
Sediment	0.04	0.02	2.00	0.02	ND	NA
Sediment	0.02	0.02	1.00	0.02	0.01	2.00
Insects	0.32	0.03	10.67	ND	ND	NA
Crayfish	0.44	ND	NA	0.01	0.01	1.00
Common Carp	2.50	ND	NA	0.20	0.02	10.00
Common Carp	1.30	ND	NA	0.12	0.03	4.00
Flathead Catfish	0.22	ND	NA	0.02	ND	NA
<u>Below the dam at Highway 166 just east of Baxter Springs</u>						
Sediment	0.06	0.06	1.00	0.03	0.02	1.50
Sediment	0.04	0.04	1.00	0.02	0.01	2.00
Insects	0.18	0.01	18.00	0.07	0.01	7.00
Crayfish	0.69	0.54	1.28	0.11	0.10	1.10
Common Carp	1.90	ND	NA	0.04	0.03	1.33
Common Carp	1.40	0.01	140.00	0.06	0.03	2.00
White Bass	3.80	0.04	95.00	0.12	0.02	6.00

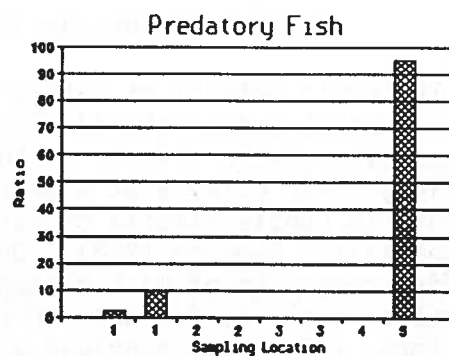
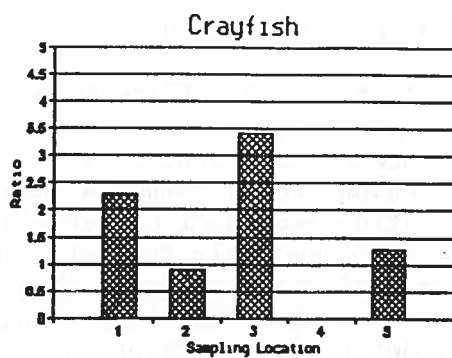


Figure 2. N-C17 to pristane ratios.

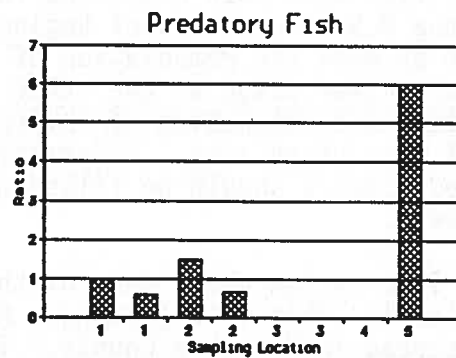
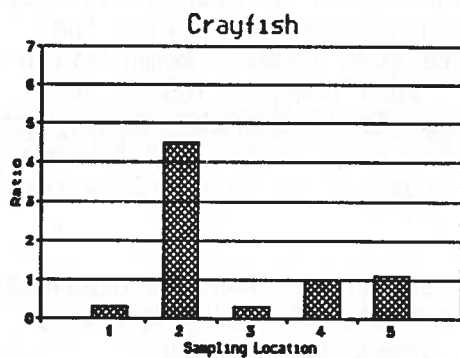


Figure 3. N-C18 to phytane ratios.

## RECOMMENDATIONS FOR FUTURE RESEARCH OR MONITORING

The toxic effects of metals in aquatic systems are difficult to assess. Metal and metalloid elements and compounds may interact to produce synergistic effects or they may counteract each other. In addition, toxic effects of metals in water "range from a complete loss of biota to subtle effects on rates of population reproduction, growth, and mortality" (Hodson 1988). Our analyses indicated only the total in the fish composite of each element for which analyses were done; the laboratory analyses did not indicate the forms of the elements present. Therefore, this study provided only indications of needed research.

Much of Cherokee County has been placed on the National Priority List for cleanup under the Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (Superfund). The Cherokee County superfund site is comprised of six subsites. A Record of Decision for remediation has been filed for the Galena subsite [U.S. Environmental Protection Agency (EPA) 1989]. Remediation predesign activities have been completed for the Galena subsite (CH2M Hill, 1990), and the U.S. Army Corps of Engineers (COE) has begun to outline the scope of work for remediation of the subsite (COE 1990). Remediation is in an earlier stage at the other subsites. Full remediation of the subsites and mitigation of environmental impacts in Cherokee County are still many years away. Information needs for both state- and federally-listed species should be filled as CERCLA remediation in Cherokee County proceeds.

Information about many of the endangered, threatened, or candidate species in Table 1 is lacking. Also, the effects of mining are very widespread in Cherokee County. Therefore, assessment of the environmental impacts due to past mining activities in Cherokee County is not possible without comprehensive surveys for many of the listed species that were present in the county.

Service concerns about environmental quality in Cherokee County are related primarily to past impacts on aquatic habitats. The Spring River drainage has been seriously damaged by past mining and probably by a variety of inorganic and organic contaminants (e.g. Ferrington *et al.* 1988, Spruill 1984, Terry 1986). Many may be unrelated to mining activities, and may be added to the aquatic systems in Missouri or in Kansas. For biota of the Spring River and the streams affected by the Galena subsite, assessment of both the effectiveness of preventive measures taken during remediation and the overall results of remediation will not be possible without monitoring of water quality in the streams and the river. Because much of the same information will be required for assessments of other subsites, we propose a monitoring program at sites on streams and on the Spring River. Water sampling should be

conducted for a minimum of one year, and the samples should be analyzed for a broad spectrum of inorganic and organic contaminants. The specific analyses will depend on a review of inputs to the drainages from sources in Missouri and Kansas.

#### NEEDS FOR WILDLIFE SURVEYS RELATED TO PAST MINING

Although there may be impacts to many of the terrestrial or riparian animal species or to the plant species listed in Table 1, Service concerns about impacts related to past mining in Cherokee County focus on the aquatic wildlife species. Though there may be impacts to trust resources at the mining locations, we believe that impacts on terrestrial species are relatively unimportant. Past surveys for the gray bat conducted in the vicinity of the Galena subsite (U.S. Fish and Wildlife Service 1989) indicated that the bats probably are not found in the area. Gray bats have not been recorded from any location in Cherokee County. The bald eagle may have been, and may continue to be, affected by metals mining activities. However, effects on this species likely are indirect and minimal.

Among the aquatic species in Table 1, the Neosho madtom is the species of greatest concern to the Service. Neosho madtoms occurred at two locations on the Spring River in Cherokee County, (U.S. Fish and Wildlife Service 1990), but Terry (1986) found no madtoms during her surveys. The Spring River and some of the tributaries in Cherokee County, need to be intensively surveyed for Neosho madtom occurrences, population levels, and habitat use. Surveys for the madtom also will provide information about many of the other species listed in Table 1.

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## APPENDIX

### STUDIES OF WATER QUALITY OR BIOTA IN SOUTHEASTERN KANSAS

Water quality in Cherokee County has been studied by the Kansas Department of Health and Environment (KDHE) (e.g. Anonymous 1980) and by the U.S. Geological Survey (Spruill 1984). Water quality monitoring in Cherokee County continues at KDHE.

Ferrington *et al.* (1988) studied metals and their possible effects in the Empire Lake area. Ferrington is continuing research into metals mobilization in Empire Lake (L. Ferrington, personal communication).

Several studies of sensitive amphibians in southeastern Kansas were conducted for the Kansas Department of Wildlife and Parks (KDW&P). Loraine (1983) assessed the status of the cave salamander (*Eurycea lucifuga*) and searched for the pickerel from (*Rana palustris*). The northern spring peeper (*Hyla crucifer*) was studied by Ptacek (1984). Miller (1985) studied the green frog (*Rana clamitans melanota*). At least one southeastern Kansas amphibian study for KDW&P is ongoing (K. Brunson, personal communication).

D. Edds and his students of Emporia State University is continuing studies of mussels, turtles, and fish in the Neosho and Spring river drainages (D. Edds, personal communication). At least 11 studies by graduate students at Pittsburg State University have added to the information about the status of aquatic systems in Cherokee County (Anderson, 1972, Bigley 1988, Bryant 1970, Fuller 1980, Gardner 1970, Haller 1966, Ikenberry 1978, Robinson 1980, Salsbury 1975, Stidham, 1975, and Terry 1986).

Numerous studies of the impacts of past mining on Tar Creek, primarily in Oklahoma, have been conducted by the Service or by EPA. Most of those studies should be available, if necessary, through other Service or EPA offices.

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